

Introduction:

reactions that go both ways

Chemical change is one of the two central concepts of chemical science, the other being *structure*. The very origins of Chemistry itself are rooted in the observations of transformations such as the combustion of wood, the freezing of water, and the winning of metals from their ores that have always been a part of human experience. It was, after all, the quest for some kind of constancy underlying change that led the Greek thinkers of around 200 BCE to the idea of elements and later to that of the atom.

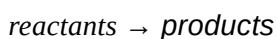
It would take almost 2000 years for the scientific study of matter to pick up these concepts and incorporate them into what would emerge, in the latter part of the 19th century, as a modern view of chemical change.

← [Rasmus Grønfeldt]

1 Chemical change: how far, how fast?

Chemical change occurs when the atoms that make up one or more substances rearrange themselves in such a way that new substances are formed. These substances are the **components** of the **chemical reaction system**; those components which decrease in quantity are called **reactants**, while those that increase are **products**.

A given chemical reaction system is defined by a **balanced net chemical equation** which is conventionally written as



The first thing we need to know about a chemical reaction represented by a balanced equation is whether it can actually take place. If the reactants and products are all substances capable of an independent existence, then in principle, the answer is always "yes". This answer must be qualified, however, by the following considerations:

How complete is the reaction?

That is, what fraction of the reactants are converted into products? Some reactions convert essentially 100% of reactants to products, while for others the quantity of products may be undetectable. Many are somewhere in between, meaning that significant quantities of all components remain at the end. Later on, in another part of the course, you will learn that the tendency of a reaction to occur can be predicted entirely from the properties of the reactants and products through the laws of thermodynamics.

How fast does the reaction occur?

Some reactions are over in microseconds; others take years. The speed of any one reaction can vary over a huge range depending on the temperature, the state of matter (gas, liquid, solid) and the presence of a catalyst. Unlike the question of completeness, there is no simple way of predicting reaction speed.

What is the mechanism of the reaction?

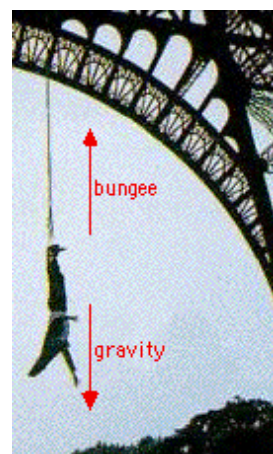
What happens, at the atomic or molecular level, when reactants are transformed into products? What intermediate species (those that are produced but later consumed so that they do not appear in the net reaction equation) are involved? This is the *microscopic*, or kinetic view of chemical change, and cannot be predicted by theory as it is presently developed and must be inferred from the results of experiments.

A reaction that is thermodynamically possible but for which no reasonably rapid mechanism is available is said to be **kinetically limited**. Conversely, one that occurs rapidly but only to a small extent is **thermodynamically limited**. As you will see later, there are often ways of getting around both kinds of limitations, and their discovery and practical applications constitute an important area of industrial chemistry.

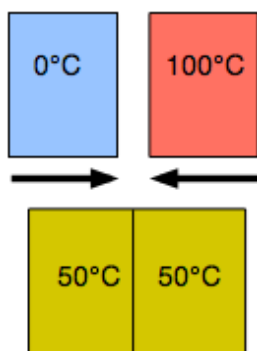
2 What is equilibrium?

Basically, the term refers to what we might call a "balance of forces". In the case of mechanical equilibrium, this is its literal definition. A book sitting on a table top remains at rest because the downward force exerted by the earth's gravity acting on the book's mass (this is what is meant by the "weight" of the book) is exactly balanced by the repulsive force between atoms that prevents two objects from simultaneously occupying the same space, acting in this case between the table surface and the book. If you pick up the book and raise it above the table top, the additional upward force exerted by your arm destroys the state of equilibrium as the book moves upward. If you wish to hold the book at rest above the table, you adjust the upward force to exactly balance the weight of the book, thus restoring equilibrium.

An object is in a state of **mechanical equilibrium** when it is either static (motionless) or in a state of unchanging motion. From the relation $f = ma$, it is apparent that if the net force on the object is zero, its acceleration must also be zero, so if we can see that an object is not undergoing a change in its motion, we know that it is in mechanical equilibrium.



Thermal equilibrium



Another kind of equilibrium we all experience is **thermal equilibrium**. When two objects are brought into contact, heat will flow from the warmer object to the cooler one until their temperatures become identical. Thermal equilibrium arises from the tendency of thermal energy to become as dispersed or "diluted" as possible.

A metallic object at room temperature will feel cool to your hand when you first pick it up because the thermal sensors in your skin detect a flow of heat from your hand into the metal, but as the metal approaches the temperature of your hand, this sensation diminishes. The time it takes to achieve thermal equilibrium depends on how readily heat is conducted within and between the objects; thus a wooden

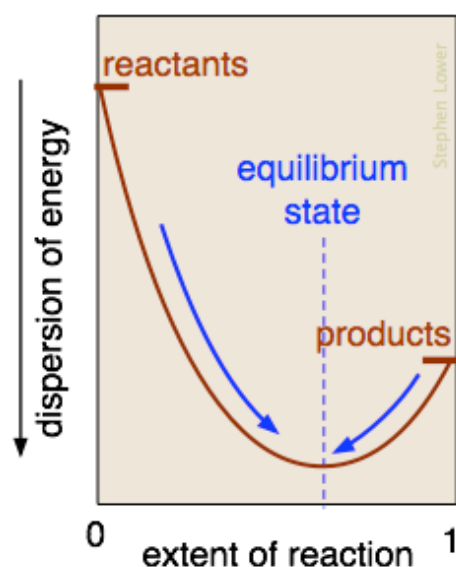
object will feel warmer than a metallic object even if both are at room temperature because wood is a relatively poor thermal conductor and will therefore remove heat from your hand more slowly.

Thermal equilibrium is something we often want to avoid, or at least postpone; this is why we insulate buildings, perspire in the summer and wear heavier clothing in the winter.

Chemical equilibrium

When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. Eventually this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its *equilibrium state*, or more simply, "at equilibrium".

Why reactions go toward equilibrium



What is the nature of the "balance of forces" that drives a reaction toward chemical equilibrium? It is essentially the balance struck between the tendency of energy to reside within the chemical bonds of stable molecules, and its tendency to become dispersed and diluted. Exothermic reactions are particularly effective in this, because the heat released gets dispersed in the infinitely wider world of the surroundings.

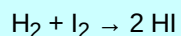
In the reaction represented here, this balance point occurs when about 60% of the reactants have been converted to products. Once this equilibrium state has been reached, no further net change will occur. (The only spontaneous changes that are allowed follow the arrows pointing toward maximum dispersal of energy.)

A more complete explanation of this must be deferred until the discussion of thermodynamics in a [later chapter](#).

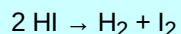
For the time being, it's very important that you know this definition:

A chemical reaction is in equilibrium when there is no tendency for the quantities of reactants and products to change.

The **direction** in which we write a chemical reaction (and thus which components are considered reactants and which are products) is arbitrary. Thus the two equations



"synthesis of hydrogen iodide"



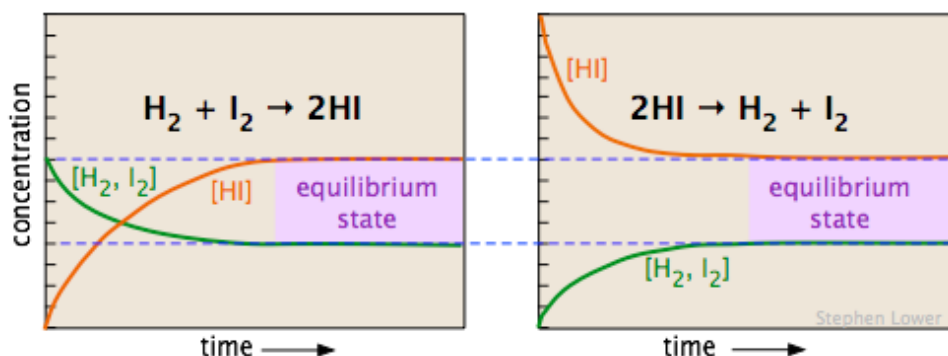
"dissociation of hydrogen iodide"

represent the same chemical reaction system in which the roles of the components are reversed, *and both yield the same mixture of components when the change is completed*.

This last point is central to the concept of chemical equilibrium. It makes no difference whether we start with two moles of HI or one mole each of H_2 and I_2 ; once the reaction has run to completion, the quantities of these two components will be the same. In general, then, we can say that the **composition of a chemical reaction system will tend to change in a direction that brings it closer to its equilibrium composition**. Once this equilibrium composition has been attained, no further change in the quantities of the components will occur as long as the system remains undisturbed.

It's the same both ways

The two diagrams below show how the concentrations of the three components of this chemical reaction change with time. Examine the two sets of plots carefully, noting which substances have zero initial concentrations, and are thus "products" of the reaction equations shown. Satisfy yourself that these two sets represent the same *chemical reaction system*, but with the reactions occurring in opposite directions. Most importantly, note how the final (equilibrium) concentrations of the components are the same in the two cases.



Whether we start with an equimolar mixture of H_2 and I_2 (left) or a pure sample of hydrogen iodide (shown on the right, using twice the initial concentration of HI to keep the number of atoms the same), the composition after equilibrium is attained (shaded regions on the right) will be the same.

The equilibrium composition is independent of the direction from which it is approached.

3 What is a reversible reaction?

A chemical equation of the form $A \rightarrow B$ represents the transformation of A into B , but it does not imply that *all* of the reactants will be converted into products, or that the *reverse* reaction $B \rightarrow A$ cannot also occur.

In general, *both* processes (forward and reverse) can be expected to occur, resulting in an *equilibrium mixture* containing finite amounts of *all* of the components of the reaction system. (We use the word *components* when we do not wish to distinguish between reactants and products.)

If the equilibrium state is one in which significant quantities of both reactants and products are present (as in the hydrogen iodide example given above), then the reaction is said to *incomplete* or **reversible**.

The latter term is preferable because it avoids confusion with "complete" in its other sense of being completed or finished, implying that the reaction has run its course and is now at equilibrium.

- If it is desired to emphasize the reversibility of a reaction, the single arrow in the equation is replaced with a pair of hooked lines pointing in opposite directions, as in $A \rightleftharpoons B$.

Note that there is no fundamental difference between the meanings of $A \rightarrow B$ and $A \rightleftharpoons B$. Some older textbooks just use $A = B$.

- A reaction is said to be *complete* or *quantitative* when the equilibrium composition contains no significant amount of the reactants. However, a reaction that is complete when written in one direction is said "not to occur" when written in the reverse direction.

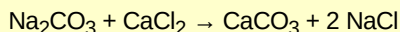
In principle, all chemical reactions are reversible, but this reversibility may not be observable if the fraction of products in the equilibrium mixture is very small, or if the reverse reaction is very slow (the chemist's term is "**kinetically inhibited**")

How did Napoleon Bonaparte help discover reversible reactions?



We can thank [Napoleon](#) for bringing the concept of reaction reversibility to Chemistry.

Napoleon recruited the eminent French chemist [Claude Louis Berthollet](#) (1748-1822) to accompany him as scientific advisor on the most far-flung of his campaigns, the [expedition into Egypt](#) in 1798. Once in Egypt, Berthollet noticed deposits of sodium carbonate around the edges of some of the salt lakes found there. He was already familiar with the reaction



which was known to proceed to completion in the laboratory. He immediately realized that the Na_2CO_3 must have been formed by the reverse of this process brought about by the very high concentration of salt in the slowly-evaporating waters. This led Berthollet to question the belief of the time that a reaction could only proceed in a single direction. His famous textbook *Essai de statique chimique* (1803) presented his speculations on chemical affinity and his discovery that an excess of the product of a reaction could drive it in the reverse direction.



Unfortunately, Berthollet got a bit carried away by the idea that a reaction could be influenced by the amounts of substances present, and maintained that the same should be true for the compositions of individual compounds. This brought him into conflict with the recently accepted Law of Definite Proportions (that a compound is made up of fixed numbers of its constituent atoms), so his ideas (the good along with the bad) were promptly discredited and remained largely forgotten for 50 years. (Ironically, it is now known that certain classes of compounds do in fact exhibit variable composition of the kind that Berthollet envisioned.)

4 What is the law of mass action?

Berthollet's ideas about reversible reactions were finally vindicated by experiments carried out by others, most notably the Norwegian chemists (and brothers-in-law) Cato Guldberg and Peter Waage. During the period 1864-1879 they showed that an equilibrium can be approached from either direction (see the hydrogen iodide illustration above), implying that any reaction

$aA + bB \rightarrow cC + dD$ is really a competition between a "forward" and a "reverse" reaction. When a reaction is at equilibrium, the rates of these two reactions are identical, so no **net** (macroscopic) change is observed, although individual components are actively being transformed at the microscopic level.

Equilibrium is *dynamic* !

The "active masses" are essentially the *concentrations* of the reactants and products that combine directly in the manner represented by the reaction equation.

The meaning of the terms on the right sides of the equations is simply that the rate is proportional to the concentrations of the components.

Guldberg and Waage showed that for a reaction $aA + bB \rightarrow cC + dD$, the rate (speed) of the reaction in either direction is proportional to what they called the "active masses" of the various components:

$$\text{rate of forward reaction} = k_f [A]^a [B]^b$$

$$\text{rate of reverse reaction} = k_r [C]^c [D]^d$$

in which the proportionality constants k are called *rate constants* and the quantities in square brackets represent concentrations. If we combine the two reactants A and B, the forward reaction starts immediately; then, as the products C and D begin to build up, the reverse process gets underway. As the reaction proceeds, the rate of the forward reaction diminishes while that of the reverse reaction increases. Eventually the two processes are proceeding at the same rate, and the reaction is at equilibrium:

$$\text{rate of forward reaction} = \text{rate of reverse reaction}$$

$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

It is very important that you understand the significance of this relation. The equilibrium state is one in which there is no **net** change in the quantities of reactants and products. But do not confuse this with a state of "no change"; at equilibrium, the forward and reverse reactions continue, but *at identical rates*, essentially cancelling each other out.

Equilibrium is macroscopically static, but is microscopically dynamic!

To further illustrate the dynamic character of chemical equilibrium, suppose that we now change the composition of the system previously at equilibrium by adding some C or withdrawing some A (thus changing their "active masses"). The reverse rate will temporarily exceed the forward rate and a change in composition ("a shift in the equilibrium") will occur until a new equilibrium composition is achieved.

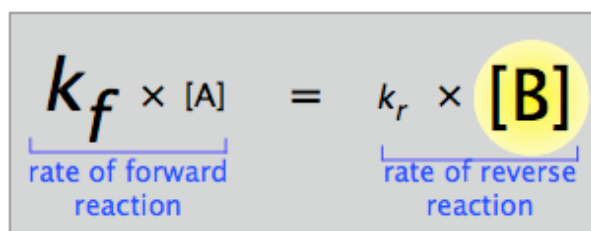
The composition of the equilibrium state depends on the ratio of the forward- and reverse rate constants.

Be sure you understand the difference between the *rate* of a reaction and a *rate constant*. The latter, usually designated by k , relates the reaction rate to the concentration of one or more of the reaction components — for example, $\text{rate} = k [\text{A}]$.

At equilibrium the rates of the forward and reverse processes are identical, but the rate *constants* are generally different. To see how this works, consider the simplified reaction $\text{A} \rightarrow \text{B}$ in the following three scenarios.

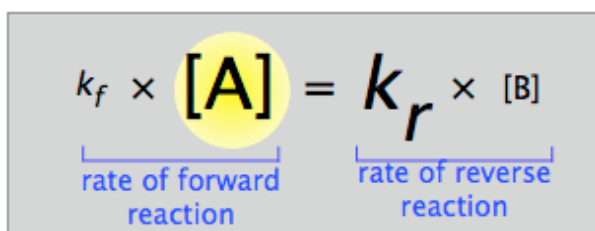
$k_f \gg k_r$

If the rate constants are greatly different (by many orders of magnitude), then this requires that the equilibrium concentrations of products exceed those of the reactants by the same ratio. Thus the equilibrium composition will lie strongly on the "right"; the reaction can be said to be "complete" or "quantitative".



$k_f \ll k_r$

The rates can only be



identical (equilibrium achieved) if the concentrations of the products are very small. We describe the resulting equilibrium as strongly favoring the left; very little product is formed. In the most extreme cases, we might even say that "the reaction does not take place".

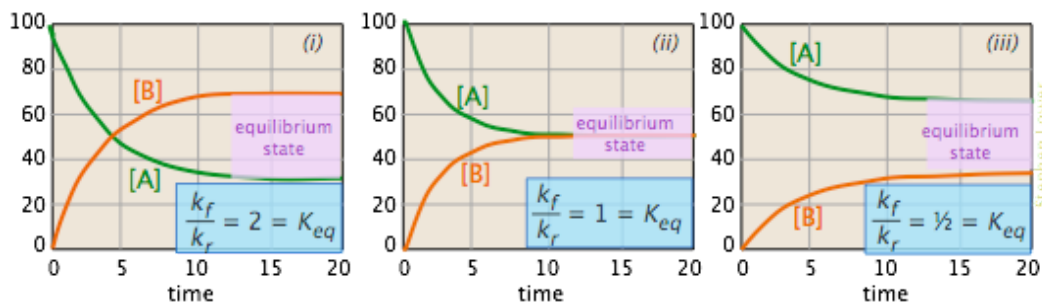
$k_f \approx k_r$

If k_f and k_r have comparable values (within, say, several orders of magnitude), then significant concentrations of products and reactants are present at equilibrium; we say the reaction is "incomplete" and "reversible".

The images shown below offer yet another way of looking at these three cases. The plots show how the relative concentrations of the reactant and product change during the course of the reaction.

The plots differ in the assumptions we make about the ratio of k_f to k_r . The equilibrium composition of the system is illustrated by the proportions of A and B in the horizontal parts of each plot where the composition remains unchanged. In each case, the two rate constants are sufficiently close in magnitude that each reaction can be considered "incomplete".

[See here](#) for a very nice online simulation that allows you to explore the effects of your own set of starting concentrations and rate constants on this kind of plot.



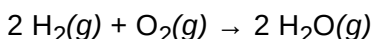
- In plot (i) the forward rate constant is twice as large as the reverse rate constant, so product (B) is favored, but there is sufficient reverse reaction to maintain a significant quantity of A.
- In (ii), the forward and reverse rate constants have identical magnitudes. Not surprisingly, so are the equilibrium values of [A] and [B].
- In (iii), the reverse rate constant exceeds the forward rate constant, so the equilibrium composition is definitely "on the left".

The Law of Mass Action is thus essentially the statement that the equilibrium composition of a reaction mixture can vary according to the quantities of components that are present. This of course is just what Berthollet observed in his Egyptian salt ponds, but we now understand it to be a consequence of the dynamic nature of chemical equilibrium.

5 How do we know when a reaction is at equilibrium?

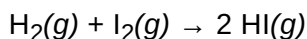
Clearly, if we observe some change taking place—a change in color, the release of gas bubbles, the appearance of a precipitate, or the release of heat, we know the reaction is not yet at equilibrium.

But the absence of any apparent change does not by itself establish that the reaction is at equilibrium. The equilibrium state is one in which not only no change in composition takes place, but also one in which no energetic tendency for further change is present. Unfortunately, "tendency" is not a property that is directly observable! Consider, for example, the reaction representing the synthesis of water from its elements:



You can store the two gaseous reactants in the same container indefinitely without any observable change occurring. But if you create an electrical spark in the container or introduce a flame, *bang!* After you pick yourself up off the floor and remove the shrapnel from what's left of your body, you will know very well that the system was not initially at equilibrium! It happens that this particular reaction has a tremendous tendency to take place, but for reasons that we will discuss in a later chapter, nothing can happen until we "set it off" in some way—in this case by exposing the mixture to a flame or spark, or (in a more gentle way) by introducing a platinum wire, which acts as a **catalyst**.

A reaction of this kind is said to be highly favored thermodynamically, but inhibited kinetically. The similar reaction of hydrogen and iodine



by contrast is only moderately favored thermodynamically (and is thus incomplete), but its kinetics are both unspectacular and reasonably facile.

Some simple tests for the equilibrium state

- As we explained above in the context of the law of mass action, addition or removal of one component of the reaction will affect the amounts of all the others. For example, if we add more of a reactant, we would expect to see the concentration of a product change. If this does not happen, then it is likely that the reaction is kinetically inhibited and that the system is unable to attain equilibrium.
- It is almost always the case, however, that once a reaction actually starts, it will continue on its own until it reaches equilibrium, so if we can observe the change as it occurs and see it slow down and stop, we can be reasonably certain that

the system is in equilibrium. This is by far the chemist's most common criterion.

- There is one other experimental test for equilibrium in a chemical reaction, although it is really only applicable to the kind of reactions we described above as being reversible. As we shall see later, the equilibrium state of a system is always sensitive to the temperature, and often to the pressure, so any changes in these variables, however, small, will temporarily disrupt the equilibrium, resulting in an observable change in the composition of the system as it moves toward its new equilibrium state.

Summary

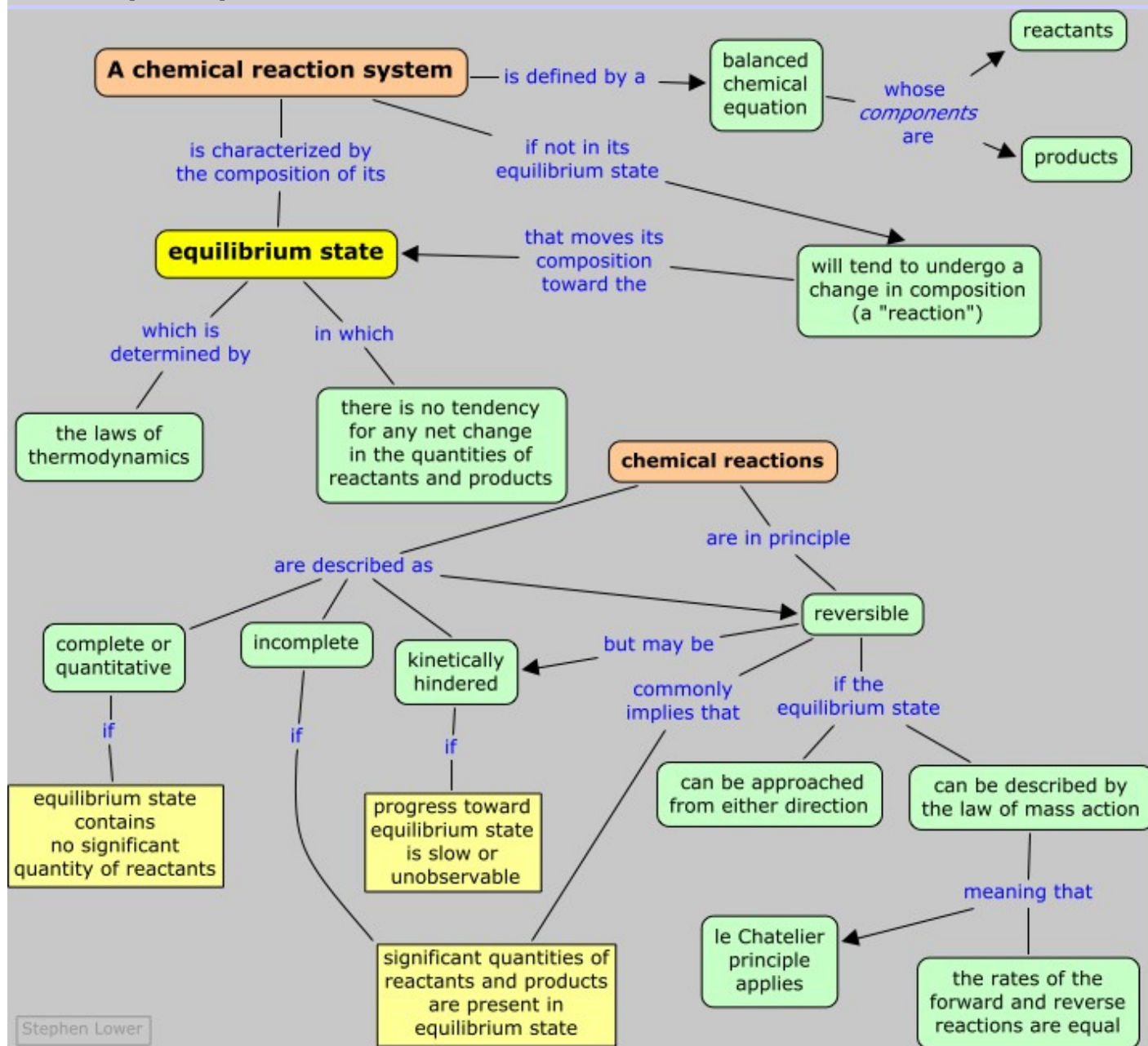
Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Any reaction that can be represented by a balanced chemical equation can take place, at least in principle. However, there are two important qualifications:
 - The tendency for the change to occur may be so small that the quantity of products formed may be very low, and perhaps negligible.
A reaction of this kind is said to be **thermodynamically inhibited**. The tendency for chemical change is governed solely by the properties of the reactants and products, and can be predicted by applying the laws of thermodynamics.
 - The rate at which the reaction proceeds may be very small, or even zero, in which case we say the reaction is **kinetically inhibited**. Reaction rates depend on the **mechanism** of the reaction— that is, on what actually happens to the atoms as reactants are transformed into products. Reaction mechanisms cannot generally be predicted, and must be worked out experimentally. Also, the same reaction may have different mechanisms under different conditions.
- As a chemical change proceeds, the quantities of the components on one side of the reaction equation will decrease, and those on the other side will increase. Eventually the reaction slows down and the composition of the system stops changing. At this point the reaction is in its **equilibrium state**, and no further change in composition will occur as long as the system is left undisturbed.
- For many reactions, the equilibrium state is one in which components on both sides of the equation (that is, both reactants and products) are present in significant amounts. Such a reaction is said to be *incomplete* or **reversible**.
- **The equilibrium composition is independent of the direction from which it is approached**; the labeling of substances as "reactants" or "products" is entirely a matter of convenience. (See the hydrogen iodide reaction plots above.)
- The **law of mass action** states that any chemical change is a competition between a *forward* reaction (left-to-right in the chemical equation) and a *reverse* reaction. The rate of each of these processes is governed by the concentrations of the substances reacting; as the reaction proceeds, these rates approach each other and at equilibrium they become identical.
- From the above, it follows that **equilibrium is a dynamic process** in which **microscopic change** (the forward and reverse reactions) continues to occur, but **macroscopic change** (changes in the quantities of substances) is absent.
- When a chemical reaction is at equilibrium, any disturbance of the system, such as a change in temperature, or addition or removal of one of the reaction components, will "shift" the composition to a new equilibrium state. This is the only unambiguous way of verifying that a reaction is at equilibrium. The fact that the composition remains static does not in itself prove that a reaction is at equilibrium, because the change may be kinetically inhibited.

What you should be able to do

- Define "the **equilibrium state** of a chemical reaction system". What is its practical significance?
- State the meaning and significance of the following terms:
 - **reversible reaction**
 - **quantitative reaction**
 - **kinetically inhibited reaction**
- Explain the meaning of the statement "equilibrium is macroscopically static, but microscopically dynamic". **Very important!**
- Explain how the relative magnitudes of the forward and reverse **reaction rate constants** in the Mass Action expression affect the equilibrium composition of a reaction system.
- Describe several things you might look for during an experiment that would help determine if a reaction system is in its equilibrium state.

Concept map



The Le Châtelier Principle

Shifting the equilibrium

The previous lesson emphasized the dynamic character of equilibrium as expressed by the Law of Mass Action. This law serves as a model explaining how the composition of the equilibrium state is affected by the "active masses" (concentrations) of reactants and products.

In this lesson, we develop the consequences of this law to answer the very practical question of how an existing equilibrium composition is affected by the addition or withdrawal of one of the components.

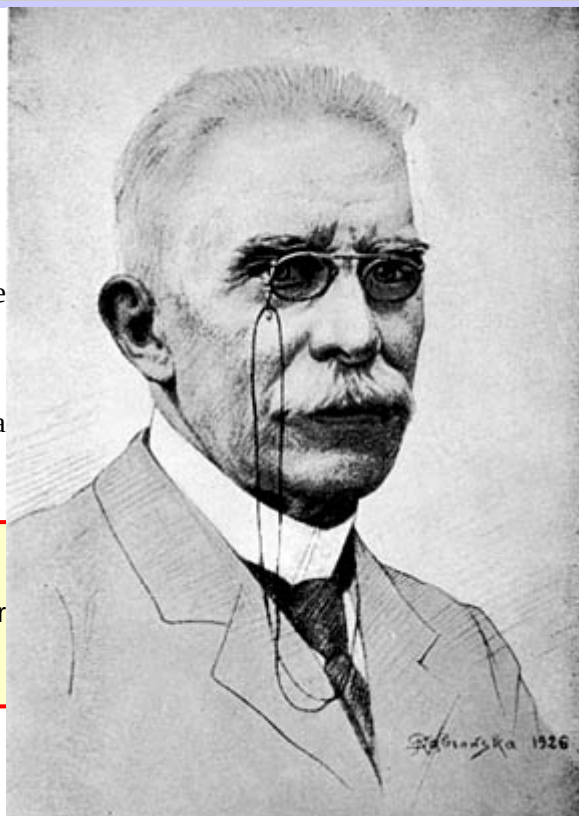
1 What is the Le Châtelier Principle?

If a reaction is at equilibrium and we alter the conditions so as to create a new **equilibrium state**, then the composition of the system will tend to change until that new equilibrium state is attained. (We say "tend to change" because if the reaction is **kinetically inhibited**, the change may be too slow to observe or it may never take place.) In 1884, the French chemical engineer and teacher **Henri Le Châtelier** (1850-1936) showed that in every such case, the new equilibrium state is one that partially reduces the effect of the change that brought it about.

This law is known to every Chemistry student as the **Le Châtelier principle**. His [original formulation](#) was somewhat complicated, but a reasonably useful paraphrase of it reads as follows:

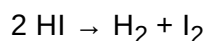
Le Châtelier principle: If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a component, there will be a tendency for a net reaction in the direction that reduces the effect of this change.

[Here it is in Le Châtelier's own \[translated\] words](#)

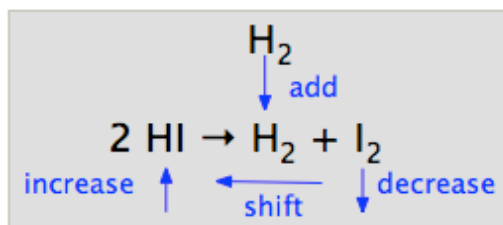


To see how this works (and you *must* do so, as this is of such fundamental importance that you simply cannot do any

meaningful chemistry without a thorough working understanding of this principle), look again at the hydrogen iodide dissociation reaction

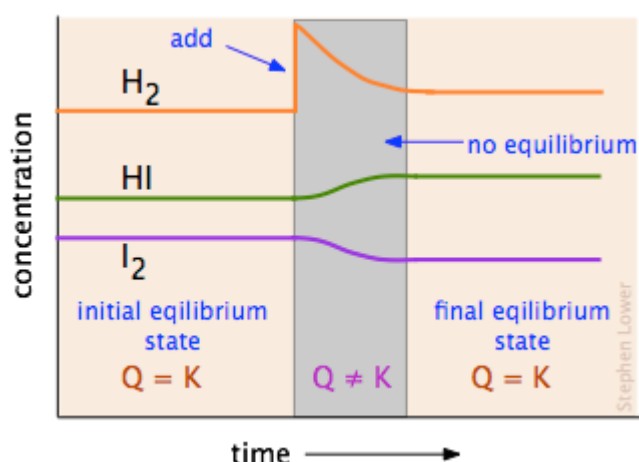


Consider an arbitrary mixture of these three components at equilibrium, and assume that we inject more hydrogen gas into the container. Because the H_2 concentration now exceeds its new equilibrium value, the system is no longer in its equilibrium state, so a net reaction now ensues as the system moves to the new state.



The Le Châtelier principle states that the net reaction will be in a direction that tends to reduce the effect of the added H_2 . This can occur if some of the H_2 is consumed by reacting with I_2 to form more HI ; in other words, a net reaction occurs in the reverse direction. Chemists usually simply say that "the equilibrium shifts to the left".

To get a better idea of how this works, carefully examine the diagram below which follows the concentrations of the three components of this reaction as they might change in time (the time scale here will typically be about an hour):



Disruption and restoration of equilibrium. At the left, the concentrations of the three components do not change with time because the system is at equilibrium. We then add more hydrogen to the system, disrupting the equilibrium. A net reaction then ensues that moves the system to a new equilibrium state (right) in which the quantity of hydrogen iodide has increased; in the process, some of the I_2 and H_2 are consumed. Notice that the new equilibrium state contains more hydrogen than did the initial state, but not as much as was added; as the Le Châtelier principle predicts, the change we made (addition of H_2) has been partially counteracted by the "shift to the right".

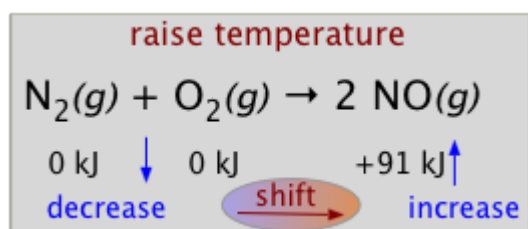
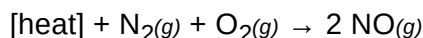
The following table contains several examples showing how changing the quantity of a reaction component can shift an established equilibrium.

system	change	result
$\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}(g) + \text{CO}$	a drying agent is added to absorb H_2O	Shift to the right. Continuous removal of a product will force any reaction to the right
$\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$	Some nitrogen gas is added	No change; N_2 is not a component of this reaction system.
$\text{NaCl}(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{Na}_2\text{SO}_4(s) + \text{HCl}(g)$	reaction is carried out in an open container	Because HCl is a gas that can escape from the system, the reaction is forced to the right . This is the basis for the commercial production of hydrochloric acid.
$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$	water evaporates from an open container	Continuous removal of water vapor forces the reaction to the right , so equilibrium is never achieved.

$\text{HCN}(aq) \rightarrow \text{H}^+(aq) + \text{CN}^-(aq)$	the solution is diluted	Shift to right ; the product $[\text{H}^+][\text{CN}^-]$ diminishes more rapidly than does $[\text{HCN}]$.
$\text{AgCl}(s) \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$	some NaCl is added to the solution	Shift to left due to increase in Cl^- concentration. This is known as the common ion effect on solubility.
$\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$	a catalyst is added to speed up this reaction	No change. Catalysts affect only the rate of a reaction; they have no effect at all on the composition of the equilibrium state.

2 How do changes in temperature affect equilibria?

Virtually all chemical reactions are accompanied by the liberation or uptake of heat. If we regard heat as a "reactant" or "product" in an endothermic or exothermic reaction respectively, we can use the Le Châtelier principle to predict the direction in which an increase or decrease in temperature will shift the equilibrium state. Thus for the oxidation of nitrogen, an endothermic process, we can write



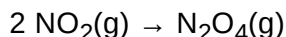
A video/lecture demonstration of the effect of temperature on the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium can be seen [here](#). See also [this brief movie](#) from Purdue U.

Suppose this reaction is at equilibrium at some temperature T_1 and we raise the temperature to T_2 . The Le Châtelier principle tells us that a net reaction will occur in the direction that will partially counteract this change. Since the reaction is endothermic, a shift of the equilibrium to the right will take place.

Nitric oxide, the product of this reaction, is a major air pollutant which initiates a sequence of steps leading to the formation of atmospheric smog. Its formation is an unwanted side reaction which occurs when the air (which is introduced into the combustion chamber of an engine to supply oxygen) gets heated to a high temperature. Designers of internal combustion engines now try, by various means, to limit the temperature in the combustion region, or to restrict its highest-temperature part to a small volume within the combustion chamber.

3 How do changes in pressure affect equilibria?

You will recall that if the pressure of a gas is reduced, its volume will increase; pressure and volume are inversely proportional. With this in mind, suppose that the reaction



is in equilibrium at some arbitrary temperature and pressure, and that we double the pressure, perhaps by compressing the mixture to a smaller volume. From the Le Châtelier principle we know that the equilibrium state will change to one that tends to counteract the increase in pressure. This can occur if some of the NO_2 reacts to form more of the dinitrogen tetroxide, since two moles of gas are being removed from the system for every mole of N_2O_4 formed, thereby decreasing the total volume of the system. Thus increasing the pressure will shift this equilibrium to the right.

It is important to understand that changing the pressure will have a significant effect only on reactions in which there is a change in the number of moles of gas.

For the above reaction, this change

$$\Delta n_g = (n_{\text{products}} - n_{\text{reactants}}) = 1 - 2 = -1.$$

In the case of the nitrogen oxidation reaction



The volumes of solids and liquids are hardly affected by the pressure at all, so for reactions that do not involve gaseous substances, the effects of pressure changes are ordinarily negligible. Exceptions arise under conditions of very high pressure such as exist in the interior of the Earth or near the bottom of the ocean. A good example is the dissolution of calcium carbonate

$\text{CaCO}_3(\text{s}) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$. There is a slight decrease in the volume when this reaction takes place, so an increase in the pressure will shift the equilibrium to the right, with the results that calcium carbonate becomes more soluble at higher pressures.

The skeletons of several varieties of microscopic organisms that inhabit the top of the ocean are made of CaCO_3 , so there is a continual rain of this substance toward the bottom of the ocean as these organisms die. As a consequence, the floor of the Atlantic ocean is covered with a blanket of calcium carbonate. This is not true for the Pacific ocean, which is deeper; once the skeletons fall below a certain depth, the higher pressure causes them to dissolve. Some of the seamounts (undersea mountains) in the Pacific extend above the solubility boundary so that their upper parts are covered with CaCO_3 sediments.

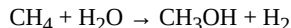
[More on marine sediments](#)

The effect of pressure on a reaction involving substances whose boiling points fall within the range of commonly encountered temperature will be sensitive to the states of these substances at the temperature of interest.

For reactions involving gases, only changes in the partial pressures of those gases directly involved in the reaction are important; the presence of other gases has no effect.

Problem example 1

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst ("steam reforming of methane"):



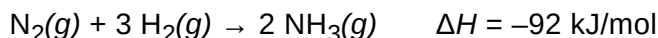
Given the following boiling points: CH_4 (methane) = -161°C , H_2O = 100°C , CH_3OH = 65° , H_2 = -253°C , predict the effects of an increase in the total pressure on this equilibrium at 50° , 75° and 120°C .

Solution: Calculate the change in the moles of gas for each process:

temp	equation	Δn_g	shift
50°	$\text{CH}_4(g) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{OH}(l) + \text{H}_2(g)$	0	none
75°	$\text{CH}_4(g) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{OH}(g) + \text{H}_2(g)$	+1	to left
120°	$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CH}_3\text{OH}(g) + \text{H}_2(g)$	0	none

4 What is the Haber process and why is it important?

The Haber process for the synthesis of ammonia is based on the exothermic reaction



The Le Châtelier principle tells us that in order to maximize the amount of product in the reaction mixture, it should be carried out at high pressure and low temperature. However, the lower the temperature, the slower the reaction (this is true of virtually all chemical reactions.) As long as the choice had to be made between a low yield of ammonia quickly or a high yield over a long period of time, this reaction was infeasible economically.

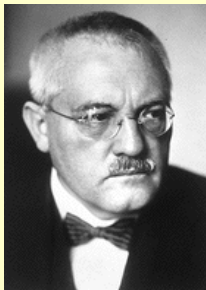
Nitrogen is available for free, being the major component of air, but the strong triple bond in N_2 makes it extremely difficult to incorporate this element into species such as NO_3^- and NH_4^+ which serve as the starting points for the wide variety of nitrogen-containing compounds that are essential for modern industry. This conversion is known as **nitrogen fixation**, and because nitrogen is an essential plant nutrient, modern intensive agriculture is utterly dependent on huge amounts of fixed nitrogen in the form of fertilizer. Until around 1900, the major source of fixed nitrogen was the NaNO_3 ([Chile saltpeter](#)) found in extensive deposits in South America. Several chemical processes for obtaining nitrogen compounds were developed in the early 1900's, but they proved too inefficient to meet the increasing demand.

Although the direct synthesis of ammonia from its elements had been known for some time, the yield of product was found to be negligible. In 1905, [Fritz Haber](#) (1868-1934) began to study this reaction, employing the thinking initiated by Le Châtelier and others, and the newly-developing field of thermodynamics that served as the basis of these principles. From the Le Châtelier law alone, it is apparent that this exothermic reaction is favored by low temperature and high pressure. However, it was not as simple as that: the rate of any reaction increases with the temperature, so working with temperature alone, one has the choice between a high product yield achieved only very slowly, or a very low yield quickly. Further, the equipment and the high-strength alloy steels

need to build it did not exist at the time. Haber solved the first problem by developing a **catalyst** that would greatly speed up the reaction at lower temperatures.

The second problem, and the development of an efficient way of producing hydrogen, would delay the practical implementation of the process until 1913, when the first plant based on the Haber-Bosch process (as it is more properly known, [Carl Bosch](#) being the person who solved the major engineering problems) came into operation. The timing could not have been better for Germany, since this country was about to enter the First World War, and the Allies had established a naval blockade of South America, cutting off the supply of nitrate for the the German munitions industry.

Bosch's plant operated the ammonia reactor at 200 atm and 550°C. Later, when stronger alloy steels had been developed, pressures of 800-1000 atm became common. The source of hydrogen in modern plants is usually natural gas, which is mostly methane:



$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$	formation of synthesis gas from methane
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	<i>shift reaction</i> carried out in reformer

The Haber-Bosch process is considered the most important chemical synthesis developed in the 20th century. Besides its scientific importance as the first large-scale application of the laws of chemical equilibrium, it has had tremendous economic and social impact; without an inexpensive source of fixed nitrogen, the intensive crop production required to feed the world's growing population would have been impossible. [Haber](#) was awarded the [1918 Nobel Prize in Chemistry](#) in recognition of his work. [Carl Bosch](#), who improved the process, won the [Nobel Prize in 1931](#).



Kathleen Duborg, Ron Halder, and David Adams
Photo by David Cooper

[Much has been written](#) about some of the more controversial and tragic aspects of Haber's life. Shown here are the major figures in the cast in the [2005 Vancouver production](#) of Vern Thiessen's play [Einstein's Gift](#) which centers on the conflict and tragedy in Fritz Haber's life. His first wife, Clara, was his former student and a chemist; Haber's decision to help Germany develop chlorine as a war gas led to her suicide.

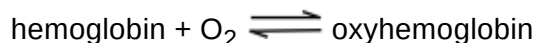
See also Thomas Hager's 2008 book *The alchemy of air; a Jewish genius, a doomed tycoon, and the scientific discovery that fed the world but fueled the rise of Hitler*.

The Le Châtelier principle in physiology

Many of the chemical reactions that occur in living organisms are regulated through the Le Châtelier principle.

Oxygen transport by the blood

Few of these are more important to warm-blooded organisms than those that relate to aerobic respiration, in which oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

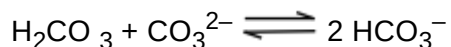


The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Much more detail about the mechanism by which hemoglobin transfers oxygen from the lungs to tissues, and then carries carbon dioxide and hydrogen ions back to the lungs, can be found on [this U. of Virginia page](#).

Maintenance of blood pH

Carbon dioxide reacts with water to form a weak acid H_2CO_3 which would cause the blood pH to fall to dangerous levels if it were not promptly removed as it is excreted by the cells. This is accomplished by combining it with carbonate ion through the reaction



which is forced to the right by the high local CO_2 concentration within the tissues. Once the hydrogen carbonate (bicarbonate) ions reach the lung tissues where the CO_2 partial pressure is much smaller, the reaction reverses and the CO_2 is expelled.

Carbon monoxide poisoning

Carbon monoxide, a product of incomplete combustion that is present in automotive exhaust and cigarette smoke, binds to hemoglobin 200 times more tightly than does O_2 . This blocks the uptake and transport of oxygen by setting up a competing equilibrium



Air that contains as little as 0.1 percent carbon monoxide can tie up about half of the hemoglobin binding sites, reducing the amount of O_2 reaching the tissues to fatal levels. Carbon monoxide poisoning is treated by administration of pure O_2 which promotes the shift of the above equilibrium to the left. This can be made even more effective by placing the victim in a hyperbaric chamber in which the pressure of O_2 can be made greater than 1 atm.

Summary

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- A system in its **equilibrium state** will remain in that state indefinitely as long as it is undisturbed. If the equilibrium is destroyed by subjecting the system to a change of pressure, temperature, or the number of moles of a substance, then a net reaction will tend to take place that moves the system to a new equilibrium state. **Le Châtelier's principle** says that this net reaction will occur in a direction that partially offsets the change.
- The Le Châtelier Principle has practical effect only for reactions in which significant quantities of both reactants and products are present at equilibrium— that is, for reactions that are **thermodynamically reversible**.
- Addition of more product substances to an equilibrium mixture will shift the equilibrium to the left; addition of more reactant substances will shift it to the right. These effects are easily explained in terms of competing forward- and reverse reactions— that is, by the **law of mass action**.
- If a reaction is **exothermic** (releases heat), an increase in the **temperature** will force the equilibrium to the left, causing the system to absorb heat and thus partially offsetting the rise in temperature. The opposite effect occurs for **endothermic** reactions, which are shifted to the right by rising temperature.
- The effect of **pressure** on an equilibrium is significant only for reactions which involve different numbers of moles of gases on the two sides of the equation. If the number of moles of gases increases, then an increase in the total pressure will tend to initiate a reverse reaction that consumes some the products, partially reducing the effect of the pressure increase.
- The classic example of the practical use of the Le Châtelier principle is the **Haber-Bosch process** for the synthesis of ammonia, in which a balance between low temperature and high pressure must be found.

References

See [here](#) for another treatment of the Le Châtelier principle.

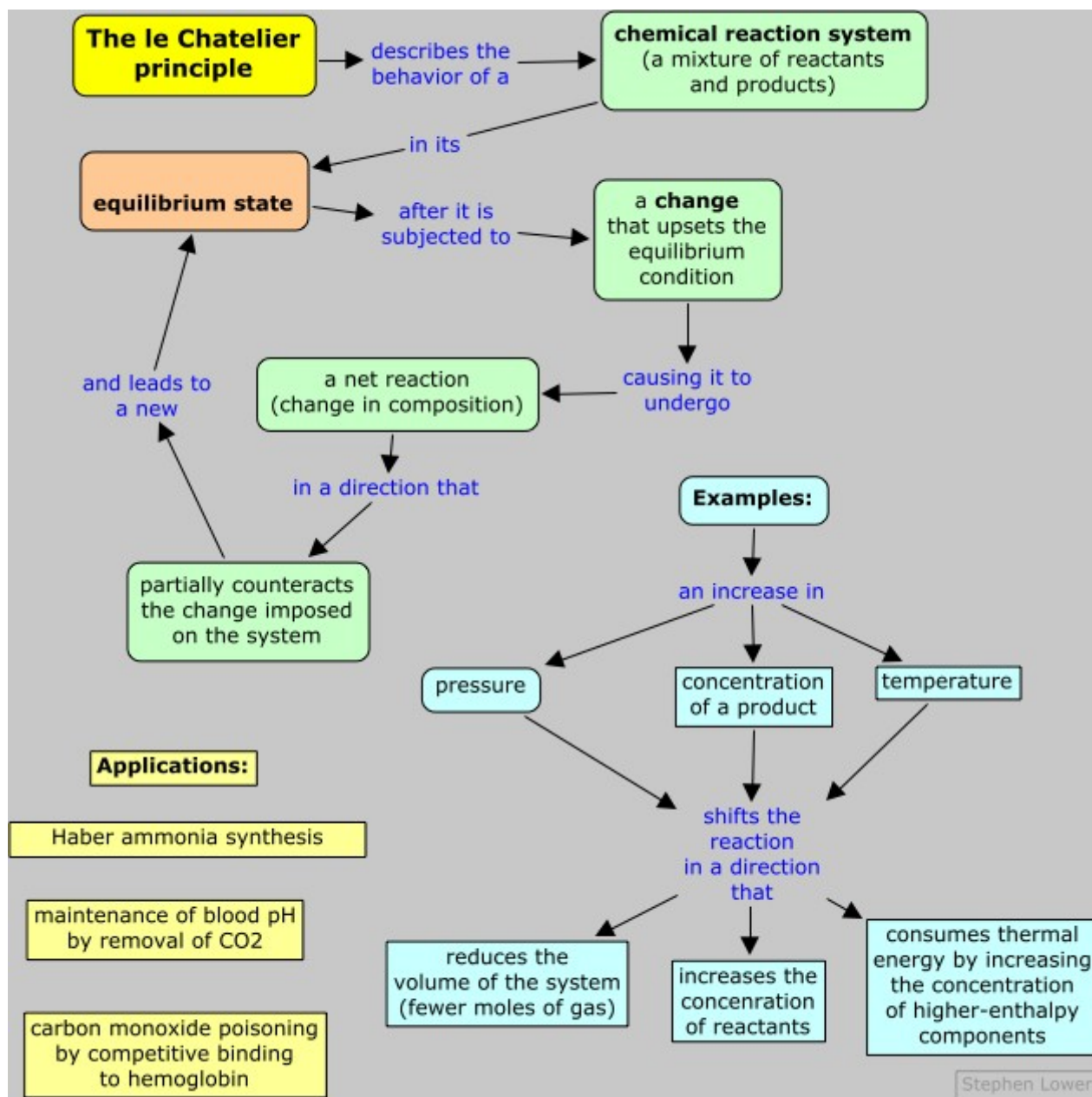
Henri Louis Le Châtelier: A man of principle - biographical sketch, including his original statement of the Principle.

Here are some [quizzes](#) to check your understanding!

Le Châtelier principle simulations

[This one](#) from Davidson U. on the water-gas reaction $\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$ allows you to explore the effects of changing all applicable variables and shows the results in a nice bar graph.

Concept Map



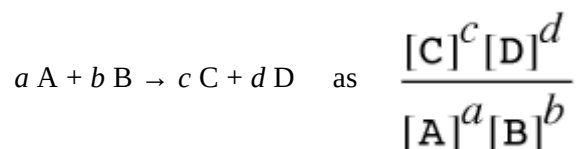
Q and K: What's the difference?

All about chemical equilibrium

Given a chemical reaction system and its equilibrium constant, together with the concentrations or pressures of the reactants and products actually present, we often need to predict whether, and in which direction, a net change in composition will tend to take place. The concept of the reaction quotient makes this very easy to do, but the similarity of the algebraic forms of K and Q can easily lead to confusion. It is hoped that the more detailed treatment offered below will help.

1 What is the equilibrium quotient?

In the previous section we defined the **equilibrium expression** for the reaction



In the general case in which the concentrations can have any arbitrary values (including zero), this expression is called the **reaction quotient** (the term *equilibrium quotient* is also commonly used.) and its value is denoted by Q (or Q_c or Q_p if we wish to emphasize that the terms represent molar concentrations or partial pressures.) If the terms correspond to *equilibrium* concentrations, then the above expression is called the **equilibrium constant** and its value is denoted by K (or K_c or K_p .)

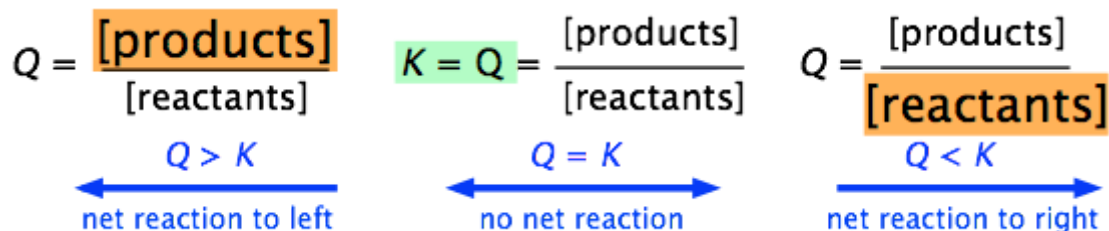
K is thus the special value that Q has when the reaction is at equilibrium

The value of Q in relation to K serves as an index how the composition of the reaction system compares to that of the equilibrium state, and thus it indicates the direction in which any net reaction must proceed.

For example, if we combine the two reactants A and B at concentrations of 1 mol L^{-1} each, the value of Q will be $0 \div 1 = 0$. The only possible change is the conversion of some of these reactants into products. If instead our mixture consists only of the two products C and D, Q will be indeterminately large ($1 \div 0$) and the only possible change will be in the reverse direction.

It is easy to see (by simple application of the le Châtelier principle) that the ratio of Q/K immediately tells us whether, and in which direction, a net reaction will occur as the system moves toward its equilibrium state. A schematic view of this relationship is shown below:

Notice the double-ended arrow in the center. This is to remind you that when the reaction is at equilibrium, the forward and reverse reactions continue as always, but at equal rates, thus cancelling each other to yield a state of no net change. (Remember the Law of Mass Action!)



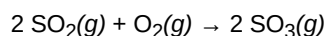
More formally, we simply look at which of the following describes the relative values of Q and K :

Q/K	
> 1	Product concentration too high for equilibrium; net reaction proceeds to left .
= 1	System is at equilibrium; no net change will occur.
< 1	Product concentration too low for equilibrium; net reaction proceeds to right .

It is very important that you be able to work out these relations for yourself, not by memorizing them, but from the definitions of Q and K .

Problem Example

The equilibrium constant for the oxidation of sulfur dioxide is $K_p = 0.14$ at 900 K.



If a reaction vessel is filled with SO_3 at a partial pressure of 0.10 atm and with O_2 and SO_2 each at a partial pressure of 0.20 atm, what can you conclude about whether, and in which direction, any net change in composition will take place?

Solution:

The value of the equilibrium quotient Q for the initial conditions is

$$Q = \frac{(p_{\text{SO}_3})^2}{(p_{\text{O}_2})(p_{\text{SO}_2})^2} = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})(0.20 \text{ atm})^2} = 1.25 \text{ atm}^{-1}$$

Since $Q > K$, the reaction is not at equilibrium, so a net change will occur in a direction that decreases Q . This can only occur if some of the SO_3 is converted back into products. In other words, the reaction will "shift to the left".

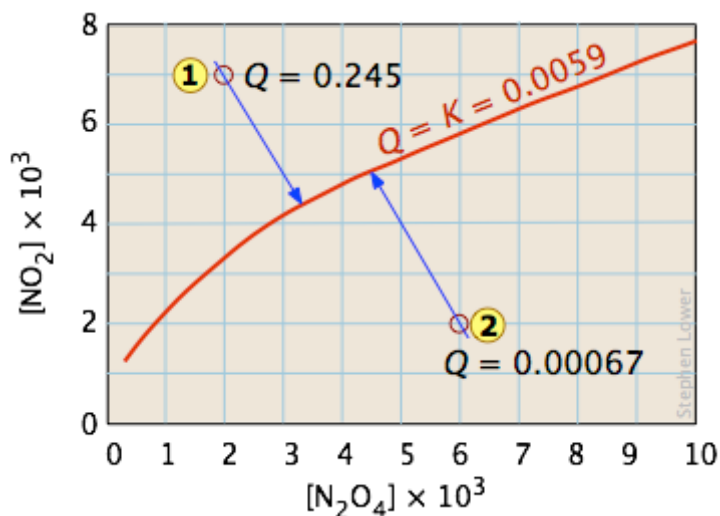
2 A visual way of thinking about Q and K

The formal definitions of Q and K are quite simple, but they are of limited usefulness unless you are able to relate them to real chemical situations. The following diagrams illustrate the relation between Q and K from various standpoints. Take some time to study each one carefully, making sure that you are able to relate the description to the illustration.

Example 1: Dissociation of dinitrogen tetroxide

For the reaction $\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$, $K_c = 0.0059$ at 298K.

This equilibrium condition is represented by the red curve that passes through all points on the graph that satisfy the



requirement that

$$Q = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4] = 0.0059 .$$

There are of course an infinite number of possible Q 's of this system within the concentration boundaries shown on the plot. Only those points that fall on the red line correspond to *equilibrium states* of this system (those for which $Q = K$). The line itself is a plot of $[\text{NO}_2]$ that we obtain by rearranging the equilibrium expression $[\text{NO}_2] = ([\text{N}_2\text{O}_4]K)^{0.5}$.

If the system is initially in a non-equilibrium state, its composition will tend to change in a direction that moves it to one that is on the line.

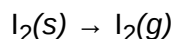
Two such non-equilibrium states are shown. The state indicated by 1 has

$Q > K$, so we would expect a net reaction that reduces Q by converting some of the NO_2 into N_2O_4 ; in other words, the equilibrium "shifts to the left". Similarly, in state 2, $Q < K$, indicating that the forward reaction will occur.

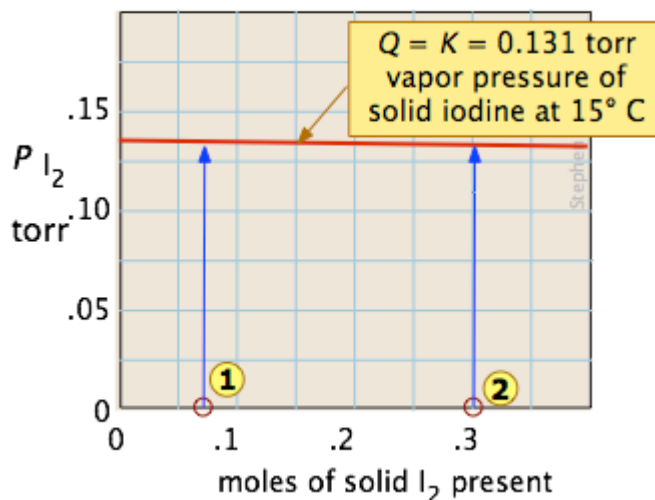
The blue arrows in the above diagram indicate the successive values that Q assumes as the reaction moves closer to equilibrium. The slope of the line reflects the stoichiometry of the equation. In this case, one mole of reactant yields two moles of products, so the slopes have an absolute value of 2:1.

Example 2: Phase-change equilibrium

One of the simplest equilibria we can write is that between a solid and its vapor. In this case (as will be explained more fully in the next lesson), the equilibrium constant is just the vapor pressure of the solid. Thus for the process



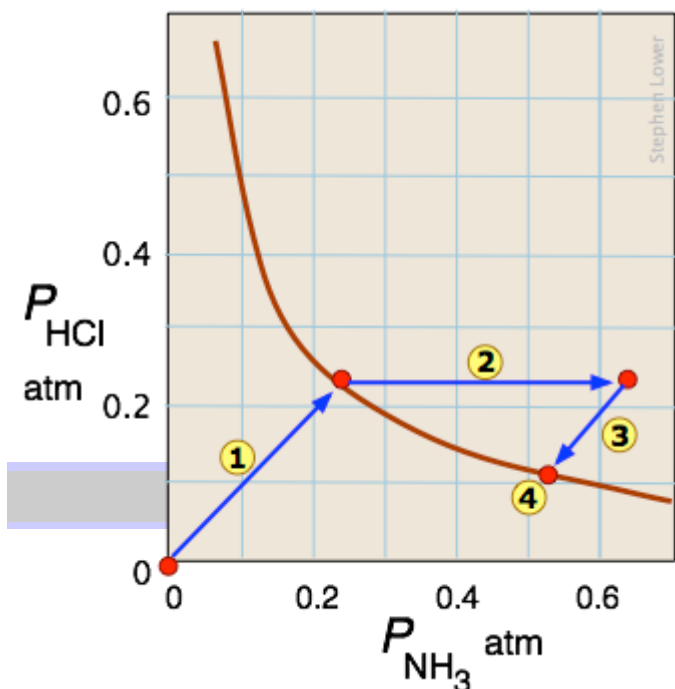
all possible equilibrium states of the system lie on the horizontal red line and is independent of the quantity of solid present (as long as there is at least enough to supply the relative tiny quantity of vapor.) So adding various amounts of the solid to an empty closed vessel (states 1 and 2) causes a gradual buildup of iodine vapor. Because the equilibrium pressure of the vapor is so small, the amount of solid consumed in the process is negligible, so the arrows go straight up and all lead to the same equilibrium vapor pressure.



Example 3: Heterogeneous chemical reaction

The decomposition of ammonium chloride is a common example of a heterogeneous (two-phase) equilibrium. Solid ammonium chloride has a substantial vapor pressure even at room temperature:





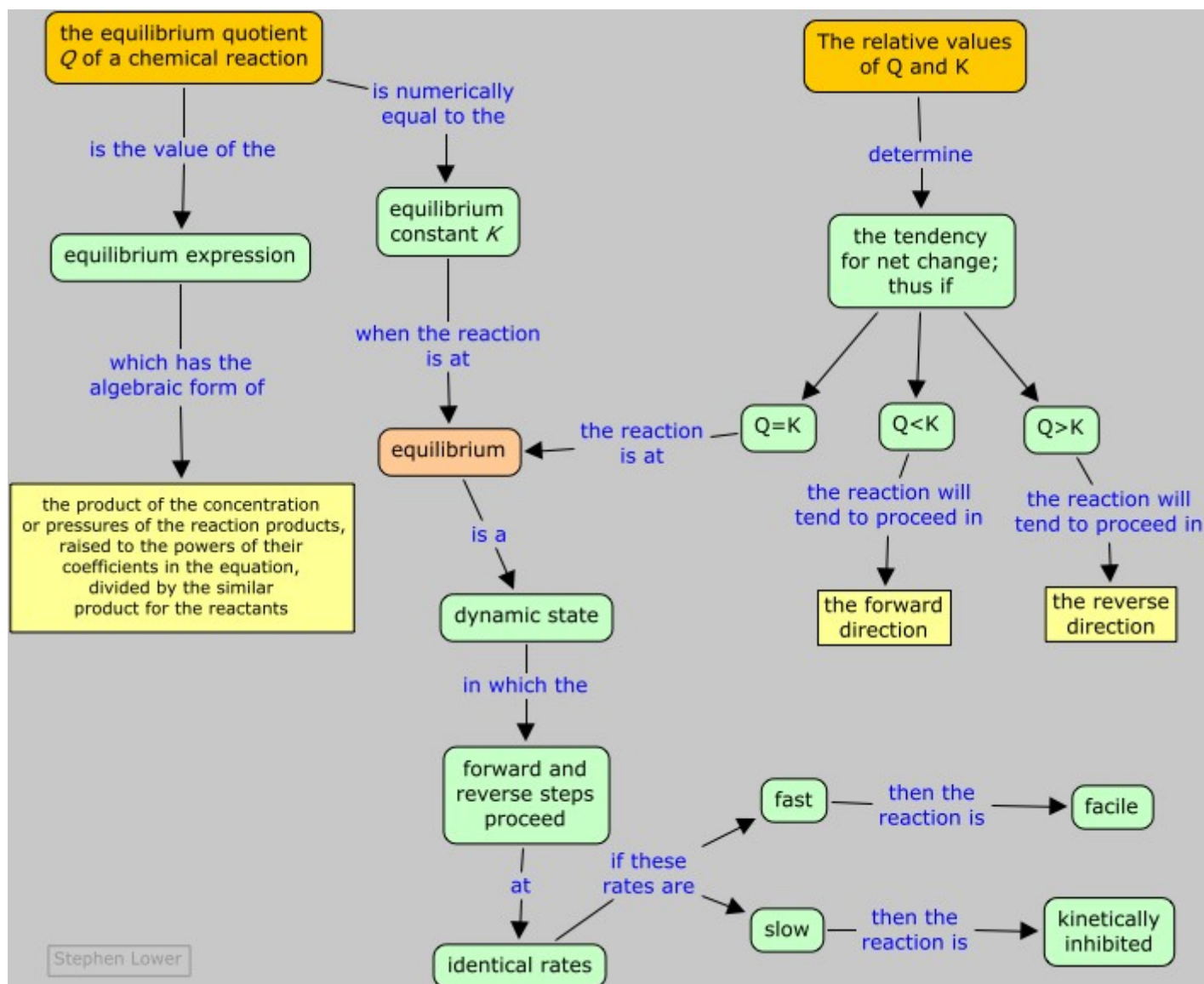
Arrow ① traces the states the system passes through when solid NH_4Cl is placed in a closed container. Arrow ② represents the addition of ammonia to the equilibrium mixture; the system responds by following the path ③ back to a new equilibrium state ④ which, as the Le Châtelier principle predicts, contains a smaller quantity of ammonia than was added. The unit slopes of the paths ① and ③ reflect the 1:1 stoichiometry of the gaseous products of the reaction.

Summary

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- When arbitrary quantities of the different **components** of a **chemical reaction system** are combined, the overall system composition will not likely correspond to the equilibrium composition. As a result, a net change in composition ("a shift to the right or left") will tend to take place until the **equilibrium state** is attained.
- The status of the reaction system in regard to its equilibrium state is characterised by the value of the **equilibrium expression** whose formulation is defined by the coefficients in the balanced reaction equation; it may be expressed in terms of concentrations, or in the case of gaseous components, as partial pressures.
- The various terms in the equilibrium expression can have any arbitrary value (including zero); the value of the equilibrium expression itself is called the **reaction quotient Q**.
- If the concentration or pressure terms in the equilibrium expression correspond to the equilibrium state of the system, then **Q** has the special value **K**, which we call the **equilibrium constant**.
- The ratio of Q/K (whether it is 1, >1 or <1) thus serves as an index of how far the system is from its equilibrium composition, and its value indicates the direction in which the net reaction must proceed in order to reach its equilibrium state.
- When $Q = K$, then the equilibrium state has been reached, and no further net change in composition will take place as long as the system remains undisturbed.

Concept Map



How to write equilibrium constant expressions

OK, you know that an equilibrium constant expression looks something like $K = [\text{products}] / [\text{reactants}]$,,, but how do you translate this into a format that relates to the actual chemical system you are interested in? This is an essential prerequisite for dealing with equilibrium calculation problems, which are treated in some detail in the unit that follows this one.

1 Pressures can express concentrations

Although we commonly write equilibrium quotients and equilibrium constants in terms of molar concentrations, any concentration-like term can be used, including mole fraction and molality. Sometimes the symbols

K_c , K_x , and K_m are used to denote these forms of the equilibrium constant. Bear in mind that the numerical values of K 's and Q 's expressed in these different ways will not generally be the same.

Most of the equilibria we deal with in this course occur in liquid solutions and gaseous mixtures. We can express K_c values in terms of moles per liter for both, but when dealing with gases it is often more convenient to use partial pressures. These two measures of concentration are of course directly proportional:

$$c = \frac{n}{V} = \frac{\frac{PV}{RT}}{V} = \frac{P}{RT}$$

so for a reaction $A(g) \rightarrow B(g)$ we can write the equilibrium constant as

$$K_p = \frac{P_B}{P_A}$$

All of these forms of the equilibrium constant are only approximately correct, working best at low concentrations or pressures. The only equilibrium constant that is truly "constant" (except that it still varies with the temperature!) is expressed in terms of **activities**, which you can think of as "effective concentrations" that allow for interactions between molecules. In practice, this distinction only becomes important for equilibria involving gases at very high pressures (such as are often encountered in chemical engineering) and in ionic solutions more concentrated than about 0.001 M. We will not deal much with activities in this course.

For a reaction such as $\text{CO}_2(g) + \text{OH}^-(aq) \rightarrow \text{HCO}_3^-(aq)$ that involves both gaseous and dissolved components, a "hybrid" equilibrium constant is commonly used:

$$K = \frac{[\text{HCO}_3^-]}{P_{\text{CO}_2} [\text{OH}^-]}$$

Clearly, it is essential to be sure of the units when you see an equilibrium constant represented simply by " K ".

Converting between K_p and K_c

It is sometimes necessary to convert between equilibrium constants expressed in different units. The most common case involves pressure- and concentration equilibrium constants.

Note that when V is expressed in liters and P in atmospheres, R must have the value 0.08206 L-atm/mol K.)

The ideal gas law relates the partial pressure of a gas to the number of moles and its volume:

$$PV = nRT$$

Concentrations are expressed in moles/unit volume n/V , so by rearranging the above equation we obtain the explicit relation of pressure to concentration:

$$P = (n/V)RT$$

Conversely, $c = (n/V) = P/RT$

... so a concentration $[A]$ can be expressed as $P_A/(RT)$.

For a reaction of the form $2 A \rightarrow B + 3 C$, we can write

$$K_p = \frac{(P_B)(P_C)^3}{(P_A)^2} = \frac{([B]RT)([C]RT)^3}{([A]RT)^2} = \underbrace{\frac{[B][C]^3}{[A]^2}}_{K_c} (RT)^{\underbrace{2}_{\Delta n_g}}$$

So in general, assuming that all of the components are gases, the relationship between the two forms of K is

$$K_p = K_c (RT)^{\Delta n_g}$$

in which Δn_g is the difference

moles of gas in products – moles of gas in reactants.

Note that for a reaction such as $2 \text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$ in which $\Delta n_g = 0$, K_p and K_c will have identical values.

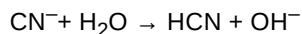
2 Don't show unchanging concentrations!

Substances whose concentrations undergo no significant change in a chemical reaction do not appear in equilibrium constant expressions.

How can the concentration of a reactant or product *not* change when a reaction involving that substance takes place? There are two general cases to consider.

The substance is also the solvent

This happens all the time in acid-base chemistry. Thus for the hydrolysis of the cyanide ion



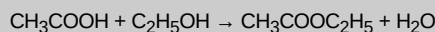
we write

$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

in which no $[\text{H}_2\text{O}]$ term appears. The justification for this omission is that water is both the solvent and reactant, but only the tiny portion that acts as a reactant would ordinarily go in the equilibrium expression. The amount of water consumed in the reaction is so minute (because K is very small) that any change in the concentration of H_2O from that of pure water (55.6 mol L^{-1}) will be negligible.

Similarly, for the "dissociation" of water $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ the equilibrium constant is expressed as the "ion product" $K_w = [\text{H}^+][\text{OH}^-]$.

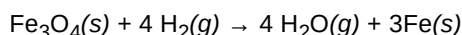
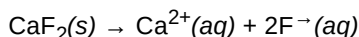
But... be careful about throwing away H_2O whenever you see it. In the esterification reaction



that we discussed in a previous section, a $[\text{H}_2\text{O}]$ term must be present in the equilibrium expression if the reaction is assumed to be between the two liquids acetic acid and ethanol. If, on the other hand, the reaction takes place between a dilute aqueous solution of the acid and the alcohol, then the $[\text{H}_2\text{O}]$ term would not be included.

The substance is a solid or a pure liquid phase.

This is most frequently seen in solubility equilibria, but there are many other reactions in which solids are directly involved:



These are **heterogeneous reactions** (meaning reactions in which some components are in different phases), and the argument here is that concentration is only meaningful when applied to a substance within a single phase.

Thus the term $[\text{CaF}_2]$ would refer to the "concentration of calcium fluoride within the solid CaF_2 ", which is a constant depending on the molar mass of CaF_2 and the density of that solid. The concentrations of the two ions will be independent of the quantity of solid CaF_2 in contact with the water; in other words, the system can be in equilibrium as long as any CaF_2 at all is present.

Throwing out the constant-concentration terms can lead to some rather sparse-looking equilibrium expressions. For example, the equilibrium expression for each of the processes shown in the following table consists solely of a single term involving the partial pressure of a gas:

1) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	$K_p = P_{\text{CO}_2}$	Thermal decomposition of limestone, a first step in the manufacture of cement.
2) $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(\text{s}) \rightarrow \text{Na}_2\text{SO}_4(\text{s}) + 10 \text{H}_2\text{O}(\text{g})$	$K_p = P_{\text{H}_2\text{O}}^{10}$	Sodium sulfate decahydrate is a solid in which H_2O molecules ("waters of hydration") are incorporated into the crystal structure.)

3) $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$	$K_p = P_{\text{I}_2}$	sublimation of solid iodine; this is the source of the purple vapor you can see above solid iodine in a closed container.
4) $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$	$K_p = P_{\text{H}_2\text{O}}$	Vaporization of water. When the partial pressure of water vapor in the air is equal to K , the relative humidity is 100%.

The last two processes 3 and 4 represent changes of state (*phase changes*) which can be treated exactly the same as chemical reactions.

In each of the heterogeneous processes shown in the table, the reactants and products can be in equilibrium (that is, permanently coexist) only when the partial pressure of the gaseous product has the value consistent with the indicated K_p . Bear in mind also that these K_p 's all increase with the temperature.

Problem Example 1

What are the values of K_p for the equilibrium between liquid water and its vapor at 25°C, 100°C, and 120°C? The vapor pressure of water at these three temperatures is 23.8 torr, 760 torr (1 atm), and 1489 torr, respectively.

Comment: These vapor pressures are the partial pressures of water vapor in equilibrium with the liquid, so they are identical with the K_p 's when expressed in units of atmospheres.

Solution:

25°C	100°C	120°C
$K_p = \frac{23.8 \text{ torr}}{760 \text{ torr atm}^{-1}} = 0.031 \text{ atm}$	$K_p = 1.00 \text{ atm}$	$K_p = \frac{1489 \text{ torr}}{760 \text{ torr atm}^{-1}} = 1.96 \text{ atm}$
The partial pressure of H_2O above the surface of liquid water in a closed container at 25°C will build up to this value. If the cover is removed so that this pressure cannot be maintained, the system will cease to be at equilibrium and the water will evaporate.	This temperature corresponds, of course, to the boiling point of water. The normal boiling point of a liquid is the temperature at which the partial pressure of its vapor is 1 atm.	The only way to heat water above its normal boiling point is to do so in a closed container that can withstand the increased vapor pressure. Thus a pressure cooker that operates at 120°C must be designed to withstand an internal pressure of at least 2 atm.

3 Values of equilibrium constants

Your ability to interpret the numerical value of a quantity in terms of what it means in a practical sense is an essential part of developing a working understanding of Chemistry. This is particularly the case for equilibrium constants, whose values span the entire range of the positive numbers.

Although there is no explicit rule, for most practical purposes you can say that equilibrium constants within the range of roughly 0.01 to 100 indicate that a chemically significant amount of all components of the reaction system will be present in an equilibrium mixture and that the reaction will be *incomplete* or “*reversible*”.

As an equilibrium constant approaches the limits of zero or infinity, the reaction can be increasingly characterized as a one-way process; we say it is “*complete*” or “*irreversible*”. The latter term must of course not be taken literally; the Le Châtelier principle still applies (especially insofar as temperature is concerned), but addition or removal of reactants or products will have less effect.

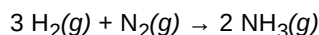
Although it is by no means a general rule, it frequently happens that reactions having very large equilibrium constants are *kinetically hindered*, often to the extent that the reaction essentially does not take place.

The examples in the following table are intended to show that numbers (values of K), no matter how dull they may look, do have practical consequences!

reaction	K	remarks
$\text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}(g)$	5×10^{-31} at 25°C, 0.0013 at 2100°C	These two very different values of K illustrate very nicely why reducing combustion-chamber temperatures in automobile engines is environmentally friendly.
$3 \text{H}_2(g) + \text{N}_2(g) \rightarrow 2 \text{NH}_3(g)$	7×10^5 at 25°C, 56 at 1300°C	See the discussion of this reaction in the section on the Haber process.
$\text{H}_2(g) \rightarrow 2 \text{H}(g)$	10^{-36} at 25°C, 6×10^{-5} at 5000°	Dissociation of any stable molecule into its atoms is endothermic. This means that all molecules will decompose at sufficiently high temperatures.
$\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$	8×10^{-41} at 25°C	You won't find water a very good source of oxygen gas at ordinary temperatures!
$\text{CH}_3\text{COOH}(l) \rightarrow$ $2 \text{H}_2\text{O}(l) + 2 \text{C}(s)$	$K_c = 10^{13}$ at 25°C	This tells us that acetic acid has a great tendency to decompose to carbon, but nobody has ever found graphite (or diamonds!) forming in a bottle of vinegar. A good example of a super kinetically-hindered reaction!

4 Do equilibrium constants have units?

The equilibrium expression for the synthesis of ammonia



can be expressed as

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \quad \text{or} \quad K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3}$$

so K_p and Q_p for this process would appear to have units of atm^{-1} , and K_c and Q_c would be expressed in $\text{mol}^{-2} \text{L}^2$. And yet these quantities are often represented as being dimensionless. Which is correct? The answer is that both forms are acceptable. There are some situations (which you will encounter later) in which K 's must be considered dimensionless, but in simply quoting the value of an equilibrium constant it is permissible to include the units, and this may even be useful in order to remove any doubt about the units of the individual terms in equilibrium expressions containing both pressure and concentration terms. In carrying out your own calculations, however, there is rarely any real need to show the units.

Strictly speaking, equilibrium expressions do not have units because the concentration or pressure terms that go into them are really *ratios* having the forms $(n \text{ mol L}^{-1})/(1 \text{ mol L}^{-1})$ or $(n \text{ atm})/(1 \text{ atm})$ in which the unit quantity in the denominator refers to the **standard state** of the substance; thus the units always cancel out. (But first-year students are not expected to know this!)

For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid, so for something like $\text{CaF}_2(\text{s})$, the term going into the equilibrium expression is $[\text{CaF}_2]/[\text{CaF}_2]$ which cancels to unity; this is the reason we don't need to include terms for solid or liquid phases in equilibrium expressions. The subject of standard states would take us beyond where we need to be at this point in the course, so we will simply say that the concept is made necessary by the fact that energy, which ultimately governs chemical change, is always relative to some arbitrarily defined zero value which, for chemical substances, is the standard state.

5 How the reaction equation affects K

It is important to remember that an equilibrium quotient or constant is always tied to a specific chemical equation, and if we write the equation in reverse or multiply its coefficients by a common factor, the value of Q or K will change.

The rules are very simple:

- Writing the equation in **reverse** will invert the equilibrium expression;
- **Multiplying** the coefficients by a common factor will raise Q or K to the corresponding power.

Here are some of the possibilities for the reaction involving the equilibrium between gaseous water and its elements:

$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$	$10 \text{H}_2 + 5 \text{O}_2 \rightarrow 10 \text{H}_2\text{O}$	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
$K_p = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}}$	$K_p = \frac{P_{\text{H}_2\text{O}}^{10}}{P_{\text{H}_2}^{10} P_{\text{O}_2}^5}$	$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}$	$K_p = \frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}}$

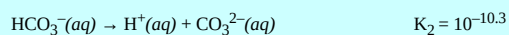
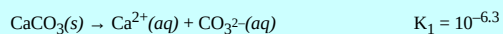
Equilibrium constant for a sequence of reactions

Many chemical changes can be regarded as the sum or difference of two or more other reactions. If we know the equilibrium constants of the individual processes, we can easily calculate that for the overall reaction according to this rule:

The equilibrium constant for the sum of two or more reactions is the product of the equilibrium constants for each of the steps.

Problem Example 2

Given the following equilibrium constants:



Calculate the value of K for the reaction $\text{CaCO}_3(s) + \text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{HCO}_3^-(aq)$

Solution: The net reaction is the sum of reaction 1 and the reverse of reaction 2:



Comment: This net reaction describes the dissolution of limestone by acid; it is responsible for the eroding effect of acid rain on buildings and statues. This is an example of a reaction that has practically no tendency to take place by itself (small K_1) being "driven" by a second reaction having a large equilibrium constant (K_{-2}). From the standpoint of the LeChâtelier principle, the first reaction is "pulled to the right" by the removal of carbonate by hydrogen ion. **Coupled** reactions of this type are widely encountered in all areas of chemistry, and especially in biochemistry, in which a dozen or so reactions may be linked.

Problem Example 3

The synthesis of HBr from hydrogen and liquid bromine has an equilibrium constant $K_p = 4.5 \times 10^{15}$ at 25°C. Given that the vapor pressure of liquid bromine is 0.28 atm, find K_p for the homogeneous gas-phase reaction at the same temperature.

Solution: The net reaction we seek is the sum of the heterogeneous synthesis of HBr and the *reverse* of the vaporization of liquid bromine:

$\text{H}_2(g) + \text{Br}_2(l) \rightarrow 2 \text{HBr}(g)$	$K_p = 4.5 \times 10^{15}$
$\text{Br}_2(g) \rightarrow \text{Br}_2(l)$	$K_p = (0.28)^{-1}$
$\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2 \text{HBr}(g)$	$K_p = 1.6 \times 10^{19}$

6 More on heterogeneous reactions

Heterogeneous reactions are those involving more than one phase. Some examples:

$\text{Fe(s)} + \text{O}_2\text{(g)} \rightarrow \text{FeO}_2\text{(s)}$	air-oxidation of metallic iron (formation of rust)
$\text{CaF}_2\text{(s)} \rightarrow \text{Ca(aq)} + \text{F}^+\text{(aq)}$	dissolution of calcium fluoride in water
$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(g)}$	sublimation of ice (a <i>phase change</i>)
$\text{NaHCO}_3\text{(s)} + \text{H}^+\text{(aq)} \rightarrow \text{CO}_2\text{(g)} + \text{Na}^+\text{(aq)} + \text{H}_2\text{O(g)}$	formation of carbon dioxide gas from sodium bicarbonate when water is added to baking powder (the hydrogen ions come from tartaric acid, the other component of baking powder.)

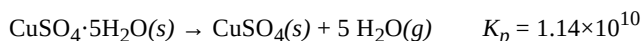
The vapor pressure of solid hydrates

A particularly interesting type of heterogeneous reaction is one in which a solid is in equilibrium with a gas. The sublimation of ice illustrated in the above table is a very common example. The equilibrium constant for this process is simply the partial pressure of water vapor in equilibrium with the solid—the **vapor pressure** of the ice.

Many common inorganic salts form solids which incorporate water molecules into their crystal structures. These water molecules are usually held rather loosely and can escape as water vapor. Copper(II) sulfate, for example forms a pentahydrate in which four of the water molecules are coordinated to the Cu^{2+} ion while the fifth is hydrogen-bonded to SO_4^{2-} . This latter water is more tightly bound, so that the pentahydrate loses water in two stages on heating:



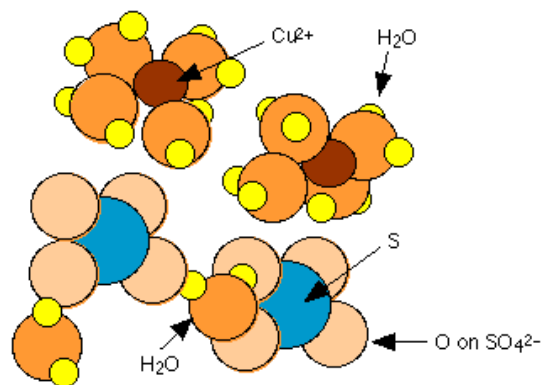
These dehydration steps are carried out at the temperatures indicated above, but at any temperature, some moisture can escape from a hydrate. For the complete dehydration of the pentahydrate we can define an equilibrium constant:



The vapor pressure of the hydrate (for this reaction) is the partial pressure of water vapor at which the two solids can coexist indefinitely; its value is $K_p^{1/5}$ atm. If a hydrate is exposed to air in which the partial pressure of water vapor is less than its vapor pressure, the reaction will proceed to the right and the hydrate will lose moisture. Vapor pressures always increase with temperature, so any of these compounds can be dehydrated by heating.

Loss of water usually causes a breakdown in the structure of the crystal; this is commonly seen with sodium sulfate, whose vapor pressure is sufficiently large that it can exceed the partial pressure of water vapor in the air when the relative humidity is low. What one sees is that the well-formed crystals of the decahydrate undergo deterioration into a powdery form, a phenomenon known as *efflorescence*.

When a solid is able to take up moisture from the air, it is described as **hygroscopic**. A small number of anhydrous solids that have low vapor pressures not only take up atmospheric moisture on even the driest of days, but will become wet as water molecules are adsorbed onto their surfaces; this is most commonly observed with sodium hydroxide and calcium chloride. With these solids, the concentrated solution that results continues to draw in water from the air so that the entire crystal eventually dissolves into a puddle of its own making; solids exhibiting this behavior are said to be **deliquescent**.



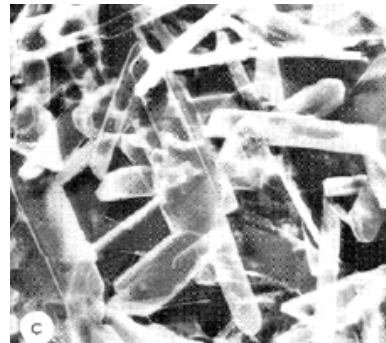
name	formula	vapor pressure, torr	
		25°C	30°C
sodium sulfate decahydrate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	19.2	25.3
copper(II) sulfate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	7.8	12.5
calcium chloride monohydrate	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	3.1	5.1
(water)	H_2O	23.5	31.6

At what relative humidity will copper sulfate pentahydrate lose its waters of hydration when the air temperature is 30°C? What is K_p for this process at this temperature?

Solution: From the table above, we see that the vapor pressure of the hydrate is 12.5 torr, which corresponds to a *relative humidity* (you remember what this is, don't you?) of $12.5/31.6 = 0.40$ or 40%. This is the humidity that will be maintained if the hydrate is placed in a closed container of dry air

For this hydrate, $K_p = P(\text{H}_2\text{O})^{0.5}$, so the partial pressure of water vapor that will be in equilibrium with the hydrate and the dehydrated solid (remember that both solids must be present to have equilibrium!), expressed in atmospheres, will be $(12.5/760)^5 = 1.20\text{E-}9$.

One of the first hydrates investigated in detail was calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) which LeChâtelier (he of the "principle") showed to be the hardened form of CaSO_4 known as *plaster of Paris*. Anhydrous CaSO_4 forms compact, powdery crystals, whereas the elongated crystals of the hemihydrate bind themselves into a cement-like mass that makes this material useful for making art objects, casts for immobilizing damaged limbs, and as a construction material (fireproofing, drywall.)

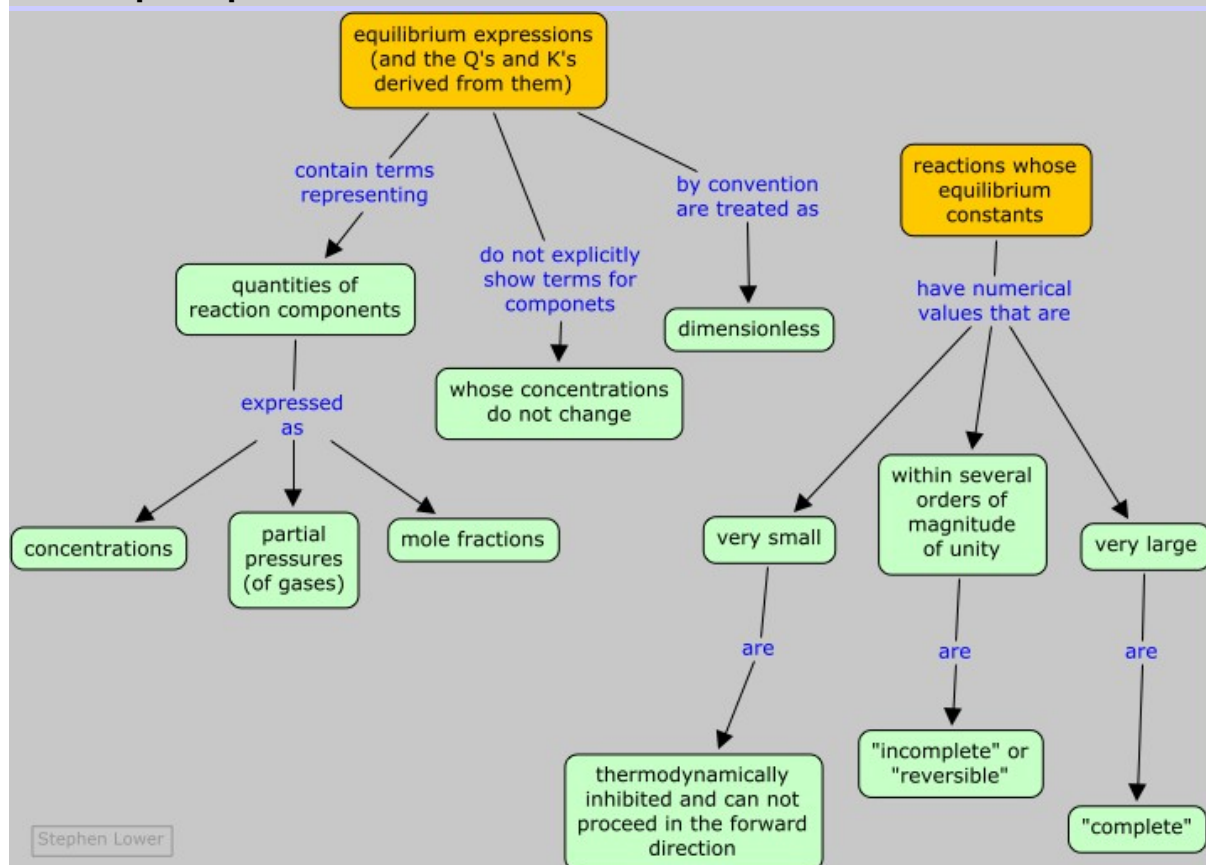


Summary

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- The **equilibrium quotient** Q is the value of the **equilibrium expression** of a reaction for any arbitrary set of concentrations or partial pressures of the reaction components.
- The **equilibrium constant** K is the value of Q when the reaction is at equilibrium. K has a unique value for a given reaction at a fixed temperature and pressure.
- Q and K can be expressed in terms of concentrations, partial pressures, or, when appropriate, in some combination of these.
- For a reaction in which all the components are gases, Q_c and K_c will have different values except in the special case in which the total number of moles of gas does not change.
- Concentration terms for substances whose concentrations do not change in the reaction do not appear in equilibrium expressions. The most common examples are $[\text{H}_2\text{O}]$ when the reaction takes place in aqueous solution (so that $[\text{H}_2\text{O}]$ is effectively constant at 55.6 M), and in heterogeneous reactions involving solids, in which the concentration of the solid is determined by the density of the solid itself.
- A reaction whose equilibrium constant is in the range of about 0.01 to 100 is said to be incomplete or [thermodynamically] **reversible**.
- Q and K are conventionally treated as dimensionless quantities, and need not ordinarily have *units* associated with them.
- **Heterogeneous** reactions are those in which two or more phases are involved; **homogeneous** reactions take place in a single phase. A common type of heterogeneous reaction is the loss of water of crystallization by a solid hydrate such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
- The equilibrium expression can be manipulated and combined in the following ways:
 - If the reaction is written in reverse, Q becomes Q^{-1} ;
 - If the coefficients of an equation are multiplied by n , Q becomes Q^n ;
 - Q for the sum of two reactions (that is, for two reactions that take place in sequence) is the *product* (Q_1)(Q_2).

Concept Map



Equilibrium calculations

Some common kinds of problems

This page presents examples that cover most of the kinds of equilibrium problems you are likely to encounter in a first-year university course.



Reading this page will **not** teach you how to work equilibrium problems! The only one who can teach you how to interpret, understand, and solve problems is **yourself**.

So don't just "read" this and think you are finished. You need to find and solve similar problems on your own. Look over the problems in your homework assignment or at the end of the appropriate chapter in a textbook, and see how they fit into the general types described below. When you can solve them without looking at the examples below, you will be well on your way!

1 Measuring and calculating equilibrium constants

Clearly, if the concentrations or pressures of all the components of a reaction are known, then the value of K can be found by simple substitution. Observing individual concentrations or partial pressures directly may be not always be practical, however. If one of the components is colored, the extent to which it absorbs light of an appropriate wavelength may serve as an index of its concentration. Pressure measurements are ordinarily able to measure only the total pressure of a gaseous mixture, so if two or more gaseous products are present in the equilibrium mixture, the partial pressure of one may need to be inferred from that of the other, taking into account the stoichiometry of the reaction.

Problem Example 1

In an experiment carried out by Taylor and Krist (*J. Am. Chem. Soc.* 1941: 1377), hydrogen iodide was found to be 22.3% dissociated at 730.8°K.

Calculate K_c for $2 \text{ HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2$.

Solution:

No explicit molar concentrations are given, but we do know that for every n moles of HI, 0.223 n moles of each product is formed and $(1-0.223)n = 0.777n$ moles of HI remains. For simplicity, we assume that $n=1$ and that the reaction is carried out in a 1.00-L vessel, so that we can substitute the required concentration terms directly into the equilibrium expression.

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.223)^2}{(0.777)^2} = 0.12$$

Problem Example 2

Ordinary white phosphorus, P_4 , forms a vapor which dissociates into diatomic molecules at high temperatures: $\text{P}_4(g) \rightarrow 2 \text{ P}_2(g)$

A sample of white phosphorus, when heated to 1000°C, formed a vapor having a total pressure of 0.20 atm and a density of 0.152 g L⁻¹. Use this information to evaluate the equilibrium constant K_p for this reaction.

Solution: Before worrying about what the density of the gas mixture has to do with K_p , start out in the usual way by laying out the information required to express K_p in terms of an unknown x .

	P_4	$2 P_2$	
initial moles:	1	$1 - x$	Since K is independent of the number of moles, assume the simplest case.
moles at equilibrium:	$1 - x$	$2x$	x is the fraction of P_4 that dissociates.
eq. mole fractions:	$\left(\frac{1 - x}{1 + x} \right)$	$\left(\frac{2x}{1 + x} \right)$	The denominator is the total number of moles: $(1-x) + 2x = 1+x$.
eq. partial pressures:	$\left(\frac{1 - x}{1 + x} \right) \times 0.2$	$\left(\frac{2x}{1 + x} \right) \times 0.2$	Partial pressure is the mole fraction times the total pressure.

Expressing the equilibrium constant in terms of x gives

$$K_p = \frac{P_{P_2}^2}{P_{P_4}} = \frac{\left(\frac{1-x}{1+x} \right)^2}{\left(\frac{2x}{1+x} \right)} = \frac{(1-x)^2}{2x}$$

Now we need to find the dissociation fraction x of P_4 , and at this point we hope you remember those gas laws that you were told you would be needing later in the course! The density of a gas is directly proportional to its molecular weight, so you need to calculate the densities of pure P_4 and pure P_2 vapors under the conditions of the experiment. One of these densities will be greater than 0.152 g L^{-1} and the other will be smaller; all you need to do is to find where the measured density falls in between the two limits, and you will have the dissociation fraction.

The molecular weight of phosphorus is 31.97, giving a molar mass of 127.9 g for P_4 . This mass must be divided by the volume to find the density; assuming ideal gas behavior, the volume of 127.9 g (1 mole) of P_4 is given by RT/P , which works out to 522 L (remember to use the absolute temperature here.) The density of pure P_4 vapor under the conditions of the experiment is then

$$d = m/V = (128 \text{ g mol}^{-1}) \times (522 \text{ L mol}^{-1}) = 0.245 \text{ g L}^{-1}.$$

The density of pure P_2 would be half this, or 0.122 g L^{-1} . The difference between these two limiting densities is 0.123 g L^{-1} , and the difference between the density of pure P_4 and that of the equilibrium mixture is $(.245 - .152) \text{ g L}^{-1}$ or 0.093 g L^{-1} . The ratio $0.093 / 0.123 = 0.76$ is therefore the fraction of P_4 that remains and its fractional dissociation is $(1 - 0.76) = 0.24$. Substituting into the equilibrium expression above gives $K_p = 1.2$.

2 Predicting equilibrium concentrations

This is by far the most common kind of equilibrium problem you will encounter: starting with an arbitrary number of moles of each component, how many moles of each will be present when the system comes to equilibrium?

The principal source of confusion and error for beginners relates to the need to determine the values of several unknowns (a concentration or pressure for each component) from a single equation, the equilibrium expression. The key to this is to make use of the stoichiometric relationships between the various components, which usually allow

us to express the equilibrium composition in terms of a single variable. The easiest and most error-free way of doing this is adopt a systematic approach in which you create and fill in a small table as shown in the following problem example. You then substitute the equilibrium values into the equilibrium constant expression, and solve it for the unknown.

This very often involves solving a quadratic or higher-order equation. Quadratics can of course be solved by using the familiar quadratic formula, but it is often easier to use an algebraic or graphical approximation, and for higher-order equations this is the only practical approach. There is almost never any need to get an exact answer, since the equilibrium constants you start with are rarely known all that precisely anyway.

Problem Example 3

Phosgene (COCl_2) is a poisonous gas that dissociates at high temperature into two other poisonous gases, carbon monoxide and chlorine. The equilibrium constant $K_p = 0.0041$ at 600°K . Find the equilibrium composition of the system after 0.124 atm of COCl_2 is allowed to reach equilibrium at this temperature.

Solution: Start by drawing up a table showing the relationships between the components:

	COCl_2	CO	Cl_2
initial pressures:	0.124 atm	0	0
change:	$-x$	$+x$	$+x$
equilibrium pressures:	$0.124 - x$	x	x

Substitution of the equilibrium pressures into the equilibrium expression gives

$$\frac{x^2}{0.124 - x} = 0.0041$$

This expression can be rearranged into standard polynomial form

$x^2 + 0.0041x - 0.00054 = 0$ and solved by the quadratic formula, but we will simply obtain an approximate solution by iteration. Because the equilibrium constant is small, we know that x will be rather small compared to 0.124, so the above relation can be approximated by

$$\frac{x^2}{0.124} = 0.0041$$

which gives $x = 0.0225$. To see how good this is, substitute this value of x into the denominator of the original equation and solve again:

$$\frac{x^2}{0.124 - 0.0225} = \frac{x^2}{0.102} = 0.0041$$

This time, solving for x gives 0.0204. Iterating once more, we get

$$\frac{x^2}{0.124 - 0.0204} = \frac{x^2}{0.104} = 0.0041$$

and $x = 0.0206$ which is sufficiently close to the previous to be considered the final result. The final partial pressures are then 0.104 atm for COCl_2 , and 0.0206 atm each for CO and Cl_2 .

Comment: using the quadratic formula to find the exact solution yields the two roots -0.0247 (which we ignore) and 0.0206, which show that our approximation is quite good.

Problem Example 4

The gas-phase dissociation of phosphorus pentachloride to the trichloride has $K_p = 3.60$ at 540°C :



What will be the partial pressures of all three components if 0.200 mole of PCl_5 and 3.00 moles of PCl_3 are combined and brought to equilibrium at this temperature and at a total pressure of 1.00 atm?

Solution: As always, set up a table showing what you know (first two rows) and then expressing the equilibrium quantities:

	PCl_5	PCl_3	Cl_2
initial moles:	0.200	3.00	0
change:	$-x$	$+x$	$+x$
equilibrium moles:	$0.200 - x$	$3.00 + x$	x
eq. partial pressures:	$\left(\frac{0.200 - x}{3.20 + x} \right)$	$\left(\frac{3.00 + x}{3.20 + x} \right)$	$\left(\frac{x}{3.20 + x} \right)$

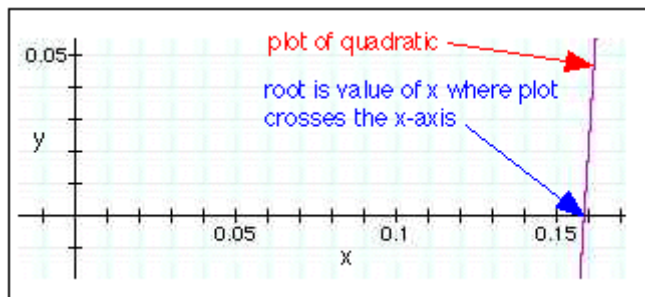
The partial pressures in the bottom row were found by multiplying the mole fraction of each gas by the total pressure: $P_i = X_i P_t$. The term in the denominator of each mole fraction is the total number of moles of gas present at equilibrium: $(0.200 - x) + (3.00 + x) + x = 3.20 + x$.

Substituting the equilibrium partial pressures into the equilibrium expression, we have

$$\frac{(3.00+x)(x)}{(0.200-x)(3.20+x)} = 3.60$$

whose polynomial form is $4.60x^2 + 13.80x - 2.304 = 0$.

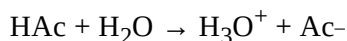
Plotting this on a graphical calculator yields $x = 0.159$ as the positive root:



Substitution of this root into the expressions for the equilibrium partial pressures in the table yields the following values: $P(\text{PCl}_5) = 0.012 \text{ atm}$, $P(\text{PCl}_3) = 0.94 \text{ atm}$, $P(\text{Cl}_2) = 0.047 \text{ atm}$.

3 Effects of dilution on equilibrium

In the section that introduced the LeChâtelier principle, it was mentioned that diluting a weak acid such as acetic acid CH_3COOH ("HAc") will shift the dissociation equilibrium to the right:



Thus a 0.10M solution of acetic acid is 1.3% ionized, while in a 0.01M solution, 4.3% of the HAc molecules will be dissociated. This is because as the solution becomes more dilute, the product $[\text{H}_3\text{O}^+][\text{Ac}^-]$ decreases more rapidly

than does the [HAc] term. At the same time the concentration of H₂O becomes greater, but because it is so large to start with (about 55.5M), any effect this might have is negligible, which is why no [H₂O] term appears in the equilibrium expression.

For a reaction such as CH₃COOH(l) + C₂H₅OH(l) → CH₃COOC₂H₅(l) + H₂O(l) (in which the water concentration does change), dilution will have no effect on the equilibrium; the situation is analogous to the way the pressure dependence of a gas-phase reaction depends on the number of moles of gaseous components on either side of the equation.

Problem Example 5

The biochemical formation of a disaccharide (double) sugar from two monosaccharides is exemplified by the reaction



(Sucrose is ordinary table sugar.) To what volume should a solution containing 0.050 mol of each monosaccharide be diluted in order to bring about 5% conversion to sucrose phosphate?

Solution: The initial and final numbers of moles are as follows:

td>

	fructose	glucose-6-P	sucrose-6-P
initial moles:	0.05	0.05	0
equilibrium moles:	0.0485	0.0485	0.0015

Substituting into the expression for K_c in which the solution volume is the unknown, we have

$$\frac{[\text{suc6P}]}{[\text{Fruc}][\text{gluc6P}]} = \frac{\left(\frac{.0485}{V}\right)}{\left(\frac{.0485}{V}\right)^2} = 0.05$$

Solving for V gives a final solution volume of **78 mL**.

4 Phase distribution equilibria

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One's first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble.

For a solute S distributed between two phases a and b the process $S_a = S_b$ is defined by the distribution law

$$K_{a,b} = \frac{[S]_a}{[S]_b}$$

in which $K_{a,b}$ is the *distribution ratio* (also called the distribution coefficient) and $[S]_i$ is the solubility of the solute in the phase.

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard "oil" phase that is almost universally used is octanol, $C_8H_{17}OH$. ([Examples](#))

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a **separatory funnel** as shown here. [image: [ransirimal](#)]

The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.

If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the LeChâtelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.

[image]



Problem Example 6

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of I_2 remaining in the aqueous phase after 50.0 mL of 0.10M I_2 in water is shaken with 10.0 mL of CS_2 .

Solution:

The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

Let m_1 and m_2 represent the numbers of millimoles of solute in the water and CS_2 layers, respectively. K_d can then be written as $(m_2/10 \text{ mL}) \div (m_1/50 \text{ mL}) = 650$. The number of moles of solute is $(50 \text{ mL}) \times (0.10 \text{ mmol mL}^{-1}) = 5.00 \text{ mmol}$, and mass conservation requires that $m_1 + m_2 = 5.00 \text{ mmol}$, so $m_2 = (5.00 - m_1) \text{ mmol}$ and we now have only the single unknown m_1 . The equilibrium constant then becomes

$$((5.00 - m_1) \text{ mmol} / 10 \text{ mL}) \div (m_1 \text{ mmol} / 50 \text{ mL}) = 650.$$

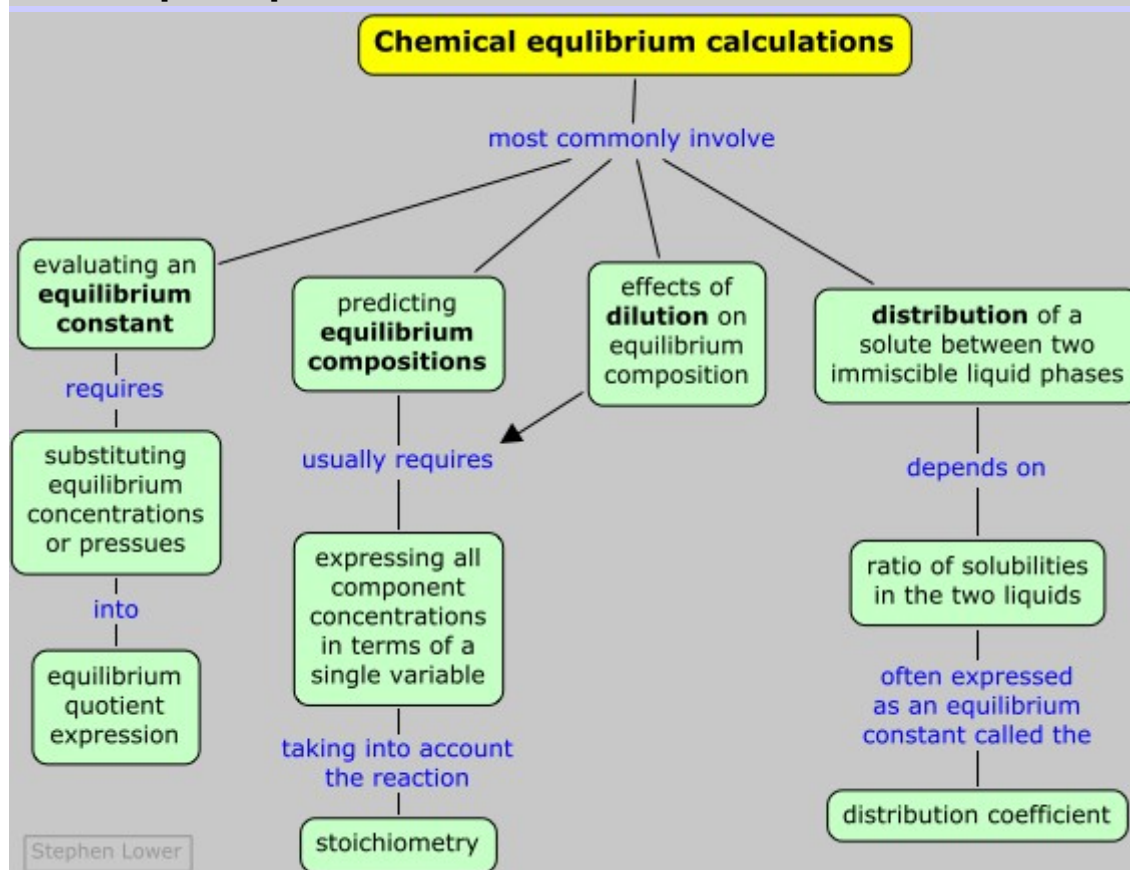
Simplifying and solving for m_1 yields $(0.50 - 0.1)m_1 / (0.02 m_1) = 650$, with $m_1 = 0.0382 \text{ mmol}$. The concentration of solute in the water layer is $(0.0382 \text{ mmol}) / (50 \text{ mL}) = \mathbf{0.000763 \text{ M}}$, showing that almost all of the iodine has moved into the CS_2 layer.

Summary

The six Problem Examples presented above were carefully selected to span the range of problem types that students enrolled in first-year college chemistry courses are expected to be able to deal with. If you are able to reproduce these solutions on your own, you should be well prepared on this topic.

- The first step in the solution of all but the simplest equilibrium problems is to sketch out a table showing for each component the *initial* concentration or pressure, the *change* in this quantity (for example, $+2x$), and the *equilibrium* values (for example, $.0036 + 2x$). In doing so, the sequence of calculations required to get to the answer usually becomes apparent.
- Equilibrium calculations often involve quadratic- or higher-order equations. Because concentrations, pressures, and equilibrium constants are seldom known to a precision of more than a few significant figures, there is no need to seek exact solutions. Iterative approximations (as in [Problem Example 3](#)) or use of a graphical calculator ([Problem Example 4](#)) are adequate and convenient.
- [Phase distribution equilibria](#) play an important role in chemical separation processes on both laboratory and industrial scales. They are also involved in the movement of chemicals between different parts of the environment, and in the bioconcentration of pollutants in the food chain.

Concept Map



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How to Solve Equilibrium Problems

Zumdahl Chapter 6 (6th Ed) Sections 1-7

Systematic Approach to following
concentrations of chemicals during a reaction

The special point of equilibrium.

Use both Q and K .

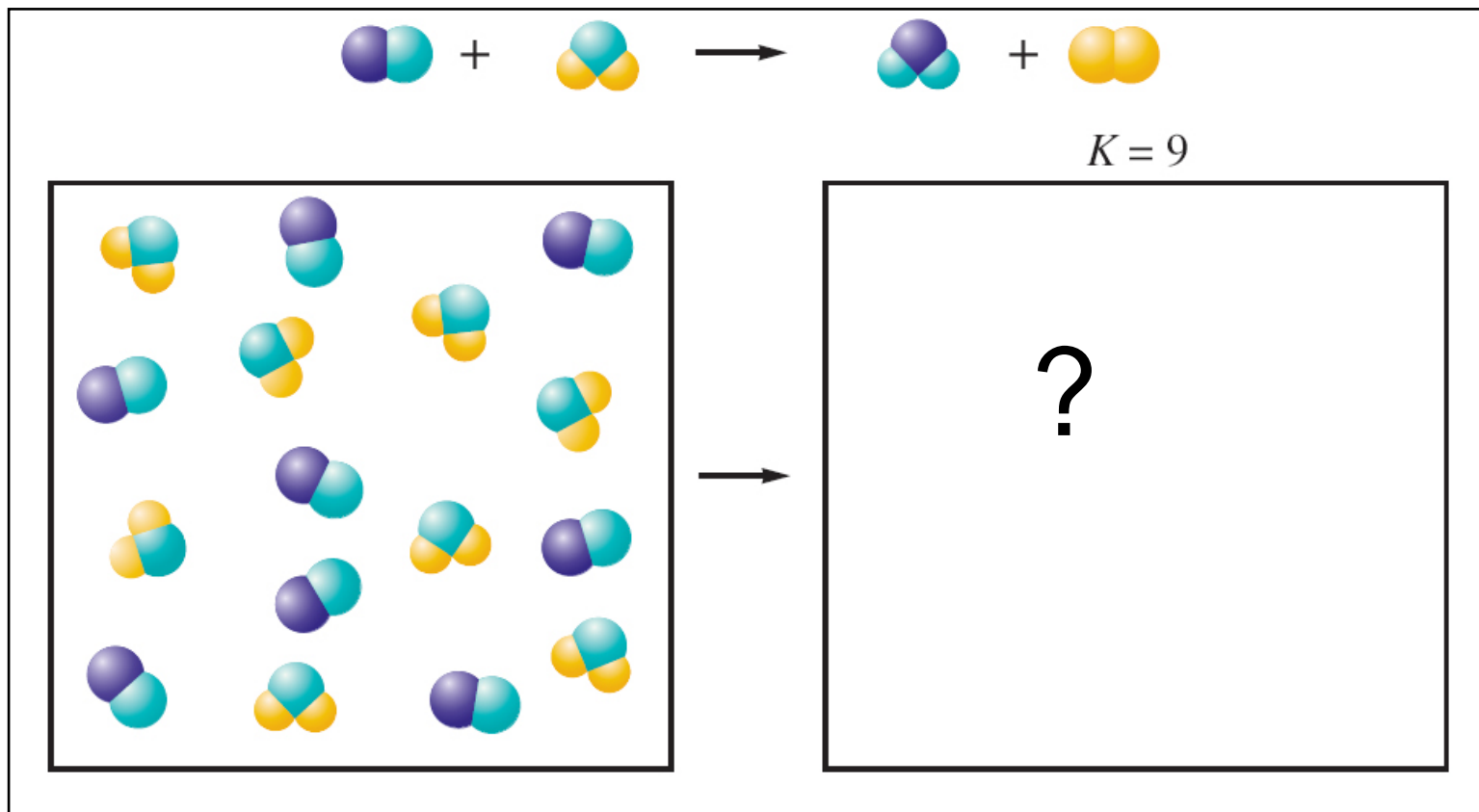
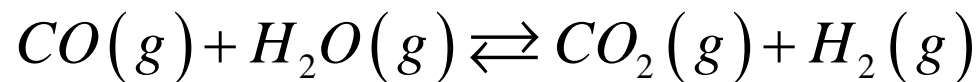
Given K , (and initial conditions) determine the
concentration of each species in a reaction.

Compare Q and K to determine the direction
of the chemical reaction.

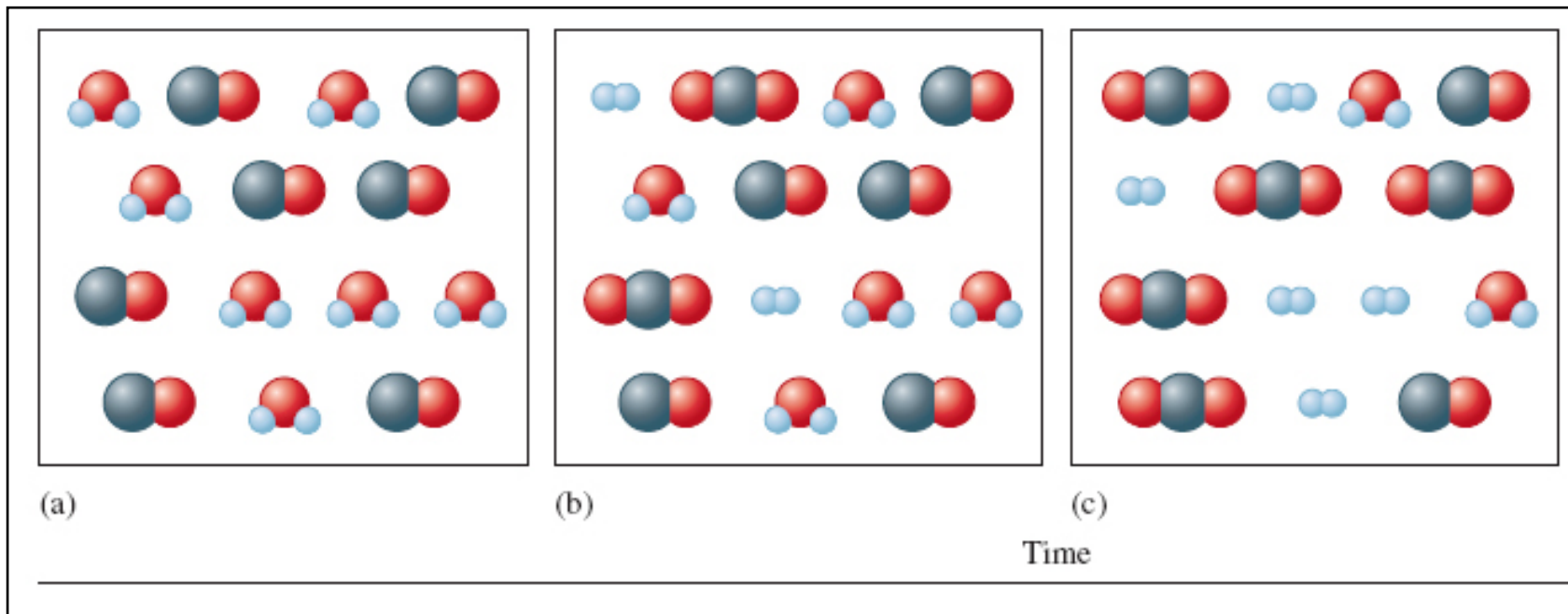
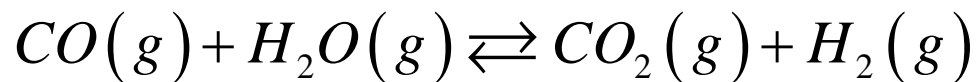
Solving Equilibrium Problems

- In the previous lecture we encountered some simple problems where we could use basic algebra to determine the value of the equilibrium constant.
- In this lecture we want to explore more complex equilibrium chemistry.
- One can view this entire lecture as introducing you to two skills:
 - Given K , determine the concentration of each and every species in the reaction at equilibrium.
 - Comparing Q and K to determine the direction in which a reaction is proceeding.

Initial Conditions for an Equilibrium Reaction

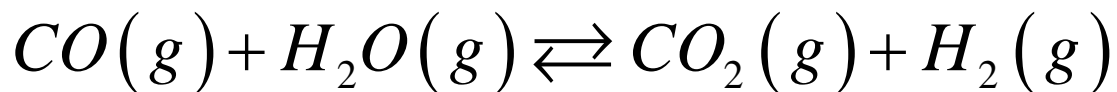


Initial Conditions for an Equilibrium Reaction



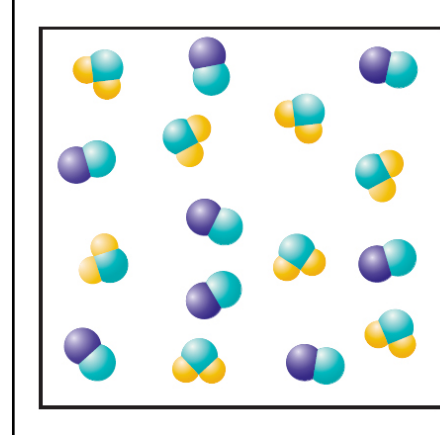
a) Initial Conditions; b) 2 Steps of the reaction ($\Delta X=2$) c) 5 Steps of reaction from start, ($\Delta X=5$). ΔX measures the change in the reaction.

Set up NICE table



Count the number of each type of molecule,

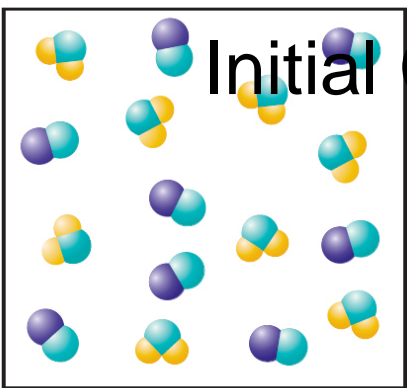
$a(CO)=8$ and $a(H_2O)=8$ at the start. No products at start



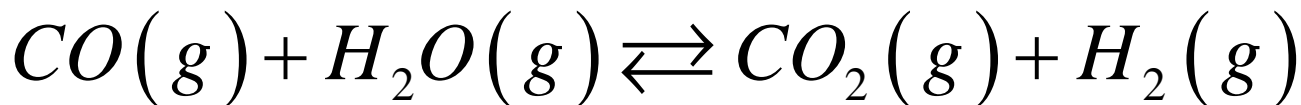
<i>Species</i>	CO	H_2O	CO_2	H_2
<i>Initial</i>	8	8	0	0
<i>Change</i>	$-\Delta X$	$-\Delta X$	ΔX	ΔX
<i>New</i>	$8 - \Delta X$	$8 - \Delta X$	ΔX	ΔX

New = Initial + Change (NIC)

At Equilibrium, we add the equilibrium condition (NICE)



Initial Conditions for an Equilibrium Reaction



Species	CO	H ₂ O	CO ₂	H ₂
---------	----	------------------	-----------------	----------------

Initial	8	8	0	0
---------	---	---	---	---

Change	$-\Delta X$	$-\Delta X$	ΔX	ΔX
--------	-------------	-------------	------------	------------

New	$8 - \Delta X$	$8 - \Delta X$	ΔX	ΔX
-----	----------------	----------------	------------	------------

$$Q = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\Delta X \cdot \Delta X}{(8 - \Delta X) \cdot (8 - \Delta X)} = \left(\frac{\Delta X}{(8 - \Delta X)} \right)^2$$

What range can ΔX take? Think of limiting reactant (or reagent).

What does $\Delta X=2$, mean?

Calculate Q for changes in reaction.

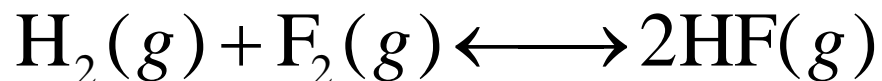
ΔX	0	2	4	6	8
$Q(\Delta X)$	0	$\frac{1}{9}$	1	9	∞

Where is Equilibrium, $K=9$?

Look at Q/K and $\log(Q/K)$.

Another Example

- Let's consider the following reaction ($K_c = 1.15 \times 10^2$):



- Initial concentrations for each species are (with subscript "0" indicating initial concentration):

$$[\text{H}_2]_0 = 1.00 \text{ M}$$

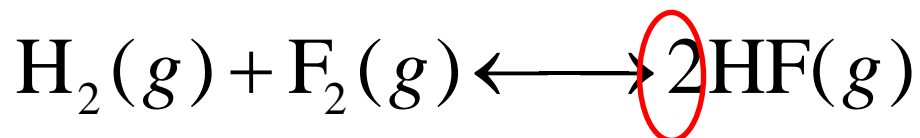
$$[\text{F}_2]_0 = 2.00 \text{ M}$$

$$[\text{HF}]_0 = 0 \text{ M}$$

- What are the concentrations of each species at equilibrium?

H₂/F₂ Example

- **First:** Make sure the reaction is balanced!

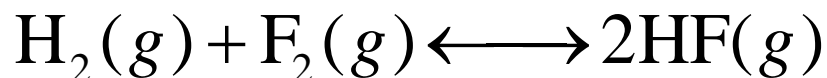


- **Second:** Construct the reaction expression:

$$Q_c = \frac{\left(\frac{[\text{HF}]}{1 \text{ M}} \right)^2}{\left(\frac{[\text{H}_2]}{1 \text{ M}} \right) \left(\frac{[\text{F}_2]}{1 \text{ M}} \right)}$$

NICE Table H2/F2

- **Third:** Using the stoichiometry of the reaction, derive expressions for concentrations at equilibrium.
- You can think through this process by considering the **initial**, **change**, and **equilibrium** concentrations. Easy to do using a “NICE” table:



Species	Initial Conc .(M)	Change in Conc. (M)	New. Conc. (M)
H ₂	1.00	-x	1.00 - x
F ₂	2.00	-x	2.00 - x
HF	0	2x	2x

Solve H₂/F₂ Equilibrium

- **Fourth:** Substitute equilibrium concentrations into the equilibrium expression and solve.

$$Q_c = \frac{\left(\frac{[\text{HF}]}{1 \text{ M}} \right)^2}{\left(\frac{[\text{H}_2]}{1 \text{ M}} \right) \left(\frac{[\text{F}_2]}{1 \text{ M}} \right)} = K_c @ EQ$$

Species	Equilib. Conc. (M)
H ₂	1.00 - x
F ₂	2.00 - x
HF	2x

By “solve” we mean solve for x which is the amount of reaction and is used to determine concentrations!

Range on answer

$$1.15 \times 10^2 = \frac{\left(\frac{2x \text{ M}}{1 \text{ M}} \right)^2}{\left(\frac{1.00 - x \text{ M}}{1 \text{ M}} \right) \left(\frac{2.00 - x \text{ M}}{1 \text{ M}} \right)} = \frac{(2x)^2}{(1.00 - x)(2.00 - x)}$$

$$1.15 \times 10^2 (1.00 - x)(2.00 - x) = (2x)^2$$

$$(1.11 \times 10^2) x^2 + (-3.45 \times 10^2) x + (2.30 \times 10^2) = 0$$

- What is the range on X? (Limiting Reactant)
- We need to solve this last equation for x.

A quadratic equation

- The last expression is a **quadratic equation** of the form:

$$ax^2 + bx + c = 0$$

$$(1.11 \times 10^2)x^2 + (-3.45 \times 10^2)x + (2.30 \times 10^2) = 0$$

- The solution to this equation can be determined using the **quadratic formula**:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

- And before you even ask....yes, you should commit to memory the quadratic formula (if you haven't already).

H2/F2 Quadratic equation

- Applying the quadratic formula to our example:

$$\begin{array}{ccc} \text{a} & \text{b} & \text{c} \\ (1.11 \times 10^2) & (-3.45 \times 10^2) & (2.30 \times 10^2) \end{array} x^2 + x + = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-3.45 \times 10^2) \pm \sqrt{(-3.45 \times 10^2)^2 - 4(1.11 \times 10^2)(2.30 \times 10^2)}}{2(1.11 \times 10^2)}$$

$$x = 2.14, 0.968$$

- Which root is correct? The answer is the correct root is the one that makes physical sense. Recall that since $[H_2]_{eq} = 1.00 - x$. Only $x = 0.968$ makes physical sense.

Individual Species at Equilibrium

- **Last:** Using expression for x , determine the equilibrium concentrations.

$$x = 0.968$$

Species	Equilib. Conc. (M)	
H ₂	1.00 - x	\longrightarrow 3.2 x 10 ⁻² M
F ₂	2.00 - x	\longrightarrow 1.03 M
HF	2 x	\longrightarrow 1.94 M

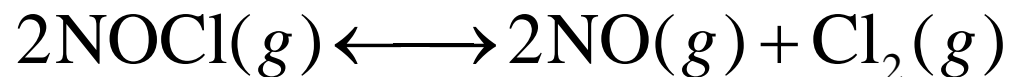
- Which species are present to the greatest extent at equilibrium? What does that tell us about the extent to which the reaction proceeds towards products?

Zumdahl's Summary: Solve Equilibrium Problems

- Write the balanced equation for the reaction.
- Write the equilibrium expression.
- List the initial concentrations.
- Define the change in concentrations using the stoichiometry of the reaction.
- Using the initial concentrations and change, write down the expressions for new concentrations.
- Substitute equilibrium concentrations into the expression for Q , and at equilibrium set $Q=K$ and solve.
- Using the physically-reasonable solution (i.e. determine limiting reagents), determine the equilibrium concentrations.

Example: NOCl Reaction

- Example. Determine the equilibrium concentrations for all species in the following reaction ($K_c = 1.60 \times 10^{-5}$).



Where the initial concentrations are:

$$[\text{NOCl}]_0 = 0.50 \text{ M}$$

$$[\text{NO}]_0 = 0 \text{ M}$$

$$[\text{Cl}_2]_0 = 0 \text{ M}$$

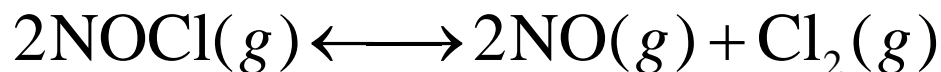
- First: Is the reaction balanced? Yes!.....and we can proceed.

NOCl Example

- Next: Write down the equilibrium constant

$$K_C = 1.60 \times 10^{-5} = Q_C = \frac{\left(\frac{[\text{NO}]}{1 \text{ M}}\right)^2 \left(\frac{[\text{Cl}_2]}{1 \text{ M}}\right)}{\left(\frac{[\text{NOCl}]}{1 \text{ M}}\right)^2}$$

- Next: NICE Table.



Species	Initial Conc .(M)	Change in Conc. (M)	New. Conc. (M)
NOCl	0.50	-2x	0.50 - 2x
NO	0	2x	2x
Cl ₂	0	x	x

NOCl Reaction

- Next: Substitute equilib. conc. expressions into K_c .

$$Q_c = \frac{\left(\frac{[\text{NO}]}{1 \text{ M}}\right)^2 \left(\frac{[\text{Cl}_2]}{1 \text{ M}}\right)}{\left(\frac{[\text{NOCl}]}{1 \text{ M}}\right)^2}$$

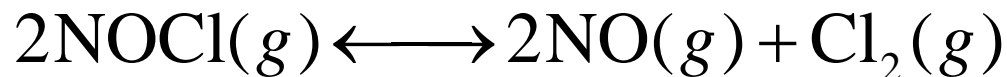
Species	Equilib. Conc. (M)
NOCl	$0.50 - 2x$
NO	$2x$
Cl_2	x

$$1.60 \times 10^{-5} = K_c = Q_c = \frac{(2x)^2 (x)}{(0.50 - 2x)^2} = \frac{4x^3}{(0.50 - 2x)^2}$$

- Wait! This isn't going to be a quadratic equation (x^3 !). What to do?

NOCl: Guess X

- Notice that $K_c = 1.60 \times 10^{-5}$ is very small. This implies that the reaction does not proceed very far towards reactants.



- We anticipate that x is very small, and that we can simply ignore the contribution x in determining the equilibrium concentration of NOCl.

Species	Equilib. Conc. (M)
NOCl	$0.50 - 2x \approx 0.50$
NO	$2x$
Cl ₂	x

$$1.60 \times 10^{-5} = \frac{4x^3}{(0.50)^2}$$

$$x = 1.00 \times 10^{-2}$$

NOCl: Guess X

- Regardless of where K is, always check by choosing an X that gives $Q < K$, (which mean too many reactants), and then a slightly larger X where $Q > K$ (too many products) Your answer is between these choices.
- Hint: This comes in very handy on multiple choice problems
- This is a very good way to test approximations.
- Valuable way to bracket your answer.
- Calculate Q at different values of X to bound X, compare Q to K.

$$K = 1.6 \cdot 10^{-5}$$

X	$0.95 \cdot 10^{-2}$	$0.98 \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$
Q	$1.5 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$

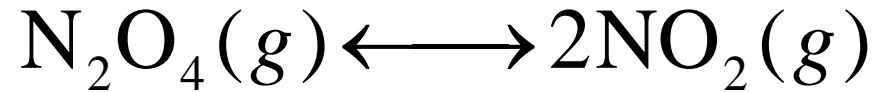
NOCl Check Approximations

- If you use this approximation, you must always go back and check the accuracy of the approximation.

Species	Equilib. Conc. (M)	Approximation (M)
NOCl	$0.50 - 2x = 0.48$	0.50
NO	$2x = 2.0 \times 10^{-2} \text{ M}$	$2.0 \times 10^{-2} \text{ M}$
Cl ₂	$x = 1.0 \times 10^{-2} \text{ M}$	$1.0 \times 10^{-2} \text{ M}$

- A few things of note:
 - Always check the validity of the approximation
 - Notice it is only the concentration of the reactant that is impacted by the approximation.
 - Use stoichiometric coefficients to get species concentrations.

Dissociation of A₂ dimer



- Example: Consider the following reaction, at 100C
- The sample starts at 0C where $K=0.133$, and $Q=K$
- The sample is heated to 100C and the system must move because now $K=67$. However Q at the start does not change, it is still 0.133, but Q will move in time as the system moves.
- We can use Q anywhere because it is defined below:
- Now $Q < K$ so the system must make more products in time.

$$Q_P = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}} \right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}} \right)}$$

A₂ Dimer Rxn: NICE Table in terms of ΔX

- NICE Table. $\text{N}_2\text{O}_4(g) \longleftrightarrow 2\text{NO}_2(g)$

Species	Initial Pres. (atm)	Change in Pres. (atm)	New. Pres. (atm)
N_2O_4	1.2	$-\Delta x$	$1.2 - \Delta x$
NO_2	0.80	$2\Delta x$	$0.80 + 2\Delta x$

$$P_{\text{N}_2\text{O}_4} = 1.2 - \Delta X$$

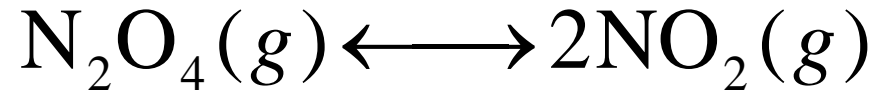
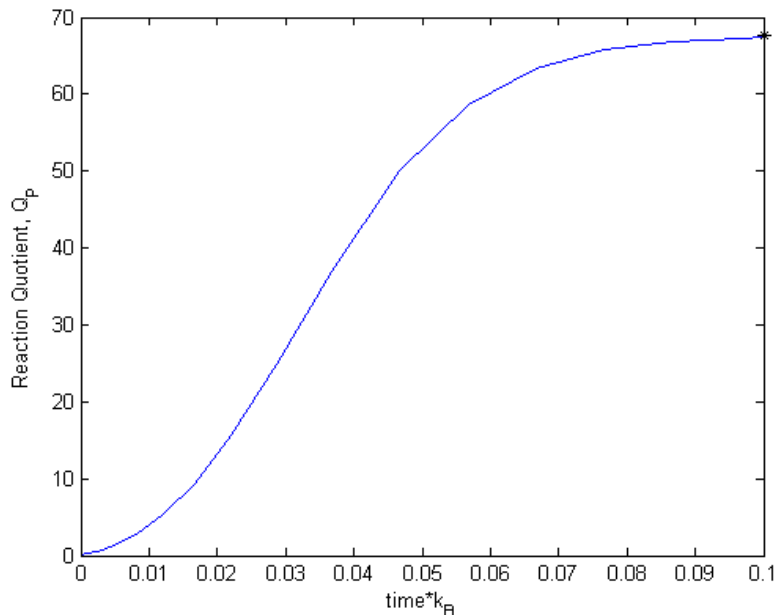
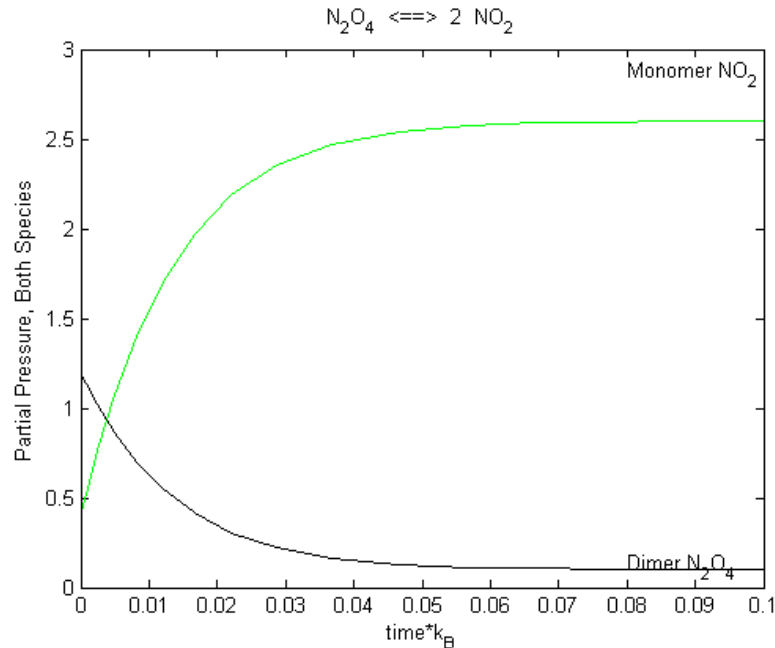
$$P_{\text{NO}_2} = 0.8 + 2\Delta X$$

- Substituting in:

$$Q(\Delta X) = \frac{(0.8 + 2\Delta X)^2}{(1.2 - \Delta X)}$$

$$Q = Q(\Delta X) = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}}\right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}}\right)} = \frac{(0.80 + 2\Delta X)^2}{(1.2 - \Delta X)}$$

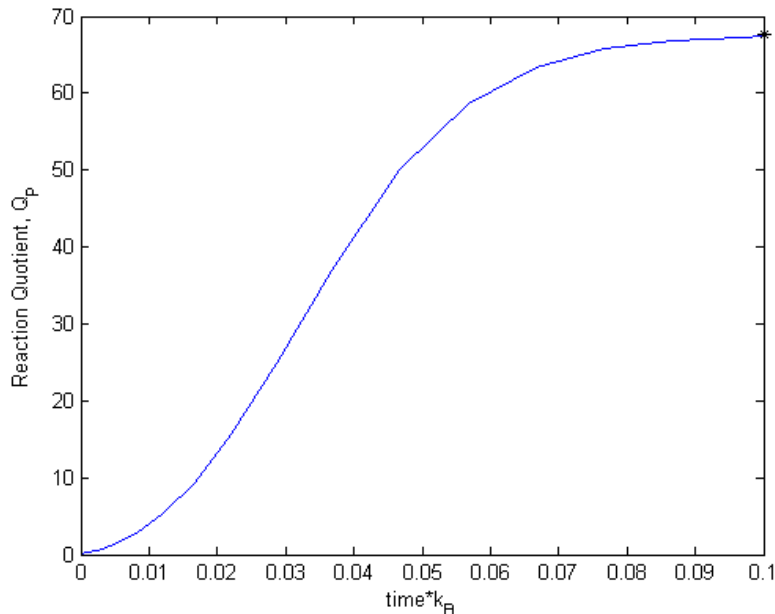
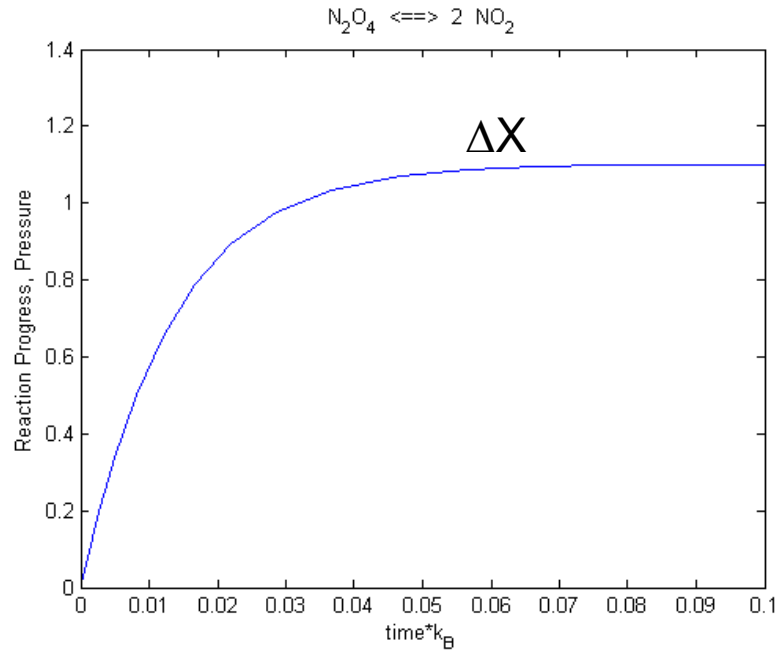
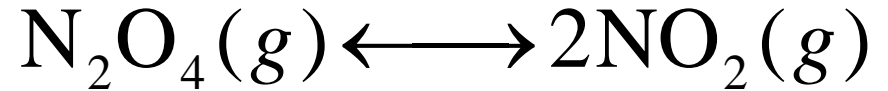
Dissociation of A₂ dimer



- Start the reaction at 0C, (K=0.133) where monomer is 0.4 Atm, and dimer is 1.2 Atm. Raise the temperature to 100C, K=67, and the system responds by making more monomer as a function of time.

$$Q = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}} \right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}} \right)}$$

Dissociation of A_2 : Reaction moves in time



- The reaction (ΔX) is the change in partial pressure and it evolves in time:

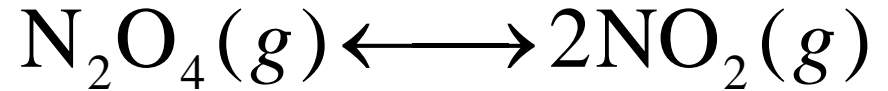
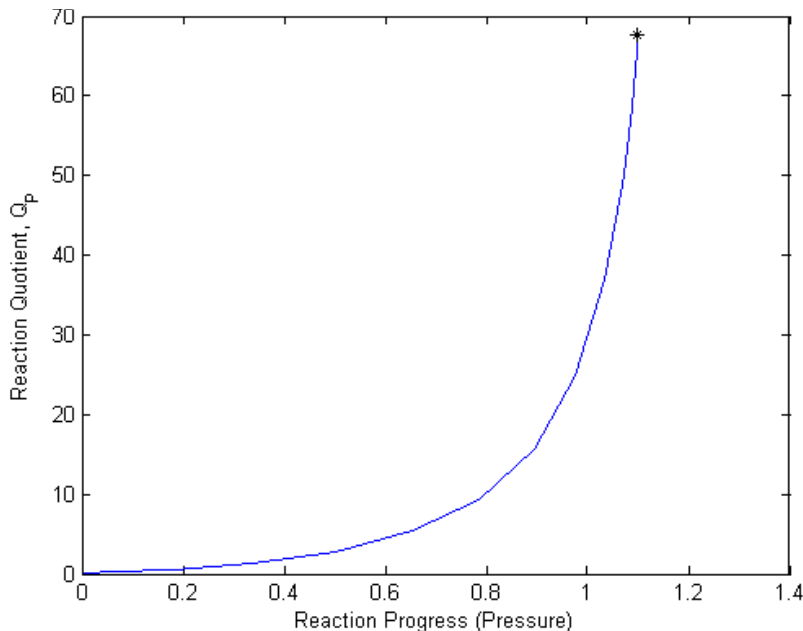
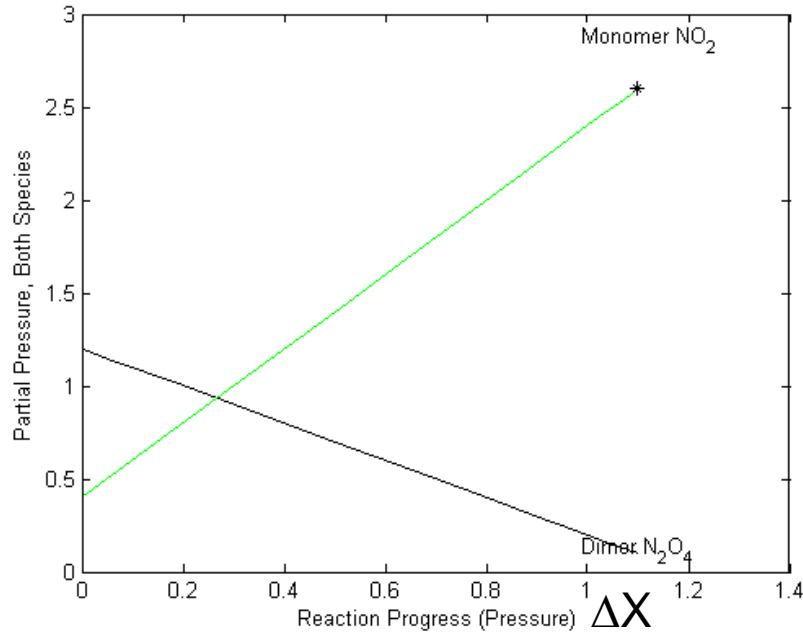
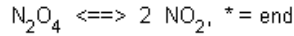
- From the NICE table

$$P_{N_2O_4} = 1.2 - \Delta X$$

$$P_{NO_2} = 0.8 + 2\Delta X$$

$$Q(\Delta X) = \frac{(0.8 + 2\Delta X)^2}{(1.2 - \Delta X)}$$

Species, and Q change with Reaction



- The reaction (ΔX) change controls the values of Q and the partial pressures of all species.

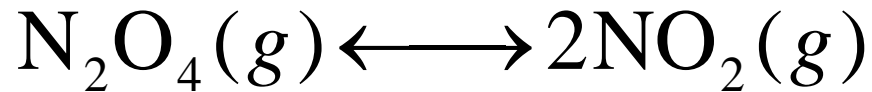
$$P_{\text{N}_2\text{O}_4} = 1.2 - \Delta X$$

$$P_{\text{NO}_2} = 0.8 + 2\Delta X$$

$$Q(\Delta X) = \frac{(0.8 + 2\Delta X)^2}{(1.2 - \Delta X)}$$

Another Example of Dissociation of A₂ dimer

- Example: Consider the following reaction ($K_p = 0.25$):



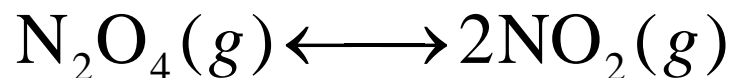
If 4.5 atm of N_2O_4 is originally placed in a container, what are the equilibrium partial pressures for both species?

- The reaction is balanced, so we can go ahead and write down the equilibrium expression:

$$K_p = 0.25 = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}}\right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}}\right)}$$

Ex: A₂ dimer dissociation

- Next: ICE Table.



Species	Initial Pres. (atm)	Change in Pres. (atm)	Equilib. Pres. (atm)
N ₂ O ₄	4.5	-x	4.5 - x
NO	0	2x	2x

- Substituting in:

$$0.25 = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}}\right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}}\right)} = \frac{(2x)^2}{(4.5 - x)} \quad \Rightarrow \quad 4x^2 + 0.25x - 1.125 = 0$$

Ex: A₂ dimer dissociation

- Determining roots of the quadratic equation:

$$4x^2 + 0.25x - 1.125 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.25 \pm \sqrt{(0.25)^2 - 4(4)(-1.125)}}{2(4)}$$

$$x = 0.5, -0.5625$$

- Inspection of the roots establishes that 0.5 is the physically reasonable solution.

Species	Initial Pres. (atm)	Change in Pres. (atm)	Equilib. Pres. (atm)
N ₂ O ₄	4.5	-x	4.5 - x = 4.0
NO	0	2x	2x = 1.0

Ex: A₂ dimer dissociation

- After equilibrium is established, 0.5 atm of N₂O₄ is injected into the container. Determine Q and the direction in which the reaction is proceeding.
- New pressures are P(N₂O₄) = 4.0 atm, P(NO₂) = 1.5 atm.
- Calculating Q:

$$Q = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}}\right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}}\right)} = \frac{(1.5)^2}{4} = 0.56 > K_p = 0.25$$

- $Q > K_p$; therefore, reaction is proceeding from products to reactants.

Ex: A_2 dimer dissociation

- What will be the new concentrations at equilibrium?
- Back to the ICE table:

Species	Initial Pres. (atm)	Change in Pres. (atm)	Equilib. Pres. (atm)
N_2O_4	4.0	-x	4.0 - x
NO	1.5	2x	1.5 + 2x

- We could have altered the sign of the change in pressure, but this will all work itself out when we look at the roots of the quadratic equation and think about what is physically reasonable.

Ex: A₂ dimer dissociation

- Put equilib. pressure expressions into K_p and solve.

$$0.25 = \frac{\left(\frac{P_{\text{NO}_2}}{1 \text{ atm}}\right)^2}{\left(\frac{P_{\text{N}_2\text{O}_4}}{1 \text{ atm}}\right)} = \frac{(1.5 + 2x)^2}{(4.0 - x)}$$

Species	Equilib. Pres. (atm)
N ₂ O ₄	4.0 - x
NO	1.5 + 2x

$$4x^2 + 6.25x + 1.25 = 0 \quad \Rightarrow \quad x = -0.235, -1.327$$

- Clearly, -0.235 is more physically realistic.

Species	Equilib. Pres. (atm)
N ₂ O ₄	4.0 - x = 4.2
NO	1.5 + 2x = 1.0